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(54) Title: ADHESION SYSTEM (57) Abstract An adhesion system for a reinforcement material and rubbers or elastomers which combines the adhesion of resorcinol-formaldehyde-latex while overcoming the environmental, safety and stability problems thereof comprises an isocyanate compound and a polyunsaturated polymer with isocyanate-reactive groups wherein the molar ratio of isocyanate groups to isocyanate reactive groups is at least 2.5:1.		

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ADHESION SYSTEM

Background of the Invention

1. Field of the Invention

5 This invention relates generally to an adhesion system for use with rubbers, synthetic elastomers and other unsaturated polymers, especially for treating fibrous and non-fibrous materials and the resultant products thereof, such as adhesive-treated fibers, yarns, fabrics and fibrous products useful as reinforcing agents and particularly to such reinforcing agents incorporated in hoses, belts, tires, molded articles, rolls and the like, as well as the resultant reinforced article.

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2. Description of the prior art

Reinforced rubber products such as tires, belts, hoses, molded articles, rolls and the like have found wide spread use for many years. These rubber products have generally been reinforced with fibrous materials in various forms such as continuous filament yarns, staple spun filament yarns, woven fabrics, knitted fabrics and other structures in order to give the rubber products the strength, flexibility and other properties needed to perform their functions. Filament yarns can be built into the composite structure by braiding, knitting, spiral wrapping and other techniques.

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Since the surface of these fiber structures are chemically different from the rubber, the compatibility of the two materials generally has been improved by an adhesive treatment to the fibrous material in order to pro-

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vide the necessary adhesion of the two materials to allow the composite structure to offer the desired advantages in properties.

The early rubber products generally included naturally occurring rubber (cis-1,4-polyisoprene plus proteins, fatty acids, lipids and numerous other naturally occurring chemicals) and synthetic rubbers, such as polyisoprene (IR), polybutadiene (BR), styrene-butadiene copolymers (SBR), acrylonitrile-butadiene copolymers (Nitrile or NR), and polychloroprene (CR or Neoprene), reinforced with naturally occurring or regenerated cellulose fibers (cotton and rayon).

One of the first and presently the most widely used adhesion treatments for these products is RFL or Resorcinol-Formaldehyde-Latex. Although there may still be some question over exactly how RFL imparts the required adhesion between the fiber and the rubber, it has been widely accepted that formaldehyde reacts with resorcinol to form methylol groups which in turn react with the hydroxyl groups of cellulose so as to provide bonding to the fiber. These methylol groups also react with specific groups in the latex, which is an aqueous dispersion of a copolymer containing rubber compatible sections such as acrylonitrile, butadiene, chloroprene and/or styrene. A reaction of specific groups of the latex polymer with the rubber is generally thought to occur during the vulcanization of the rubber.

There are many different types of rubber compounds for the many different types of rubber products. In addition to the specific type of rubber or elastomeric polymer, there are a variety of other additives such as accelerators, fillers, antidegradants, processing aids and the like designed to provide the specific properties in the rubber product. Any of these variables, including relative and absolute amounts as well as type, can affect the adhesion of a particular treated fiber product and demand

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changes in the particular ratio of R to F to L or type of L (latex polymer) and other variables in the treating procedure.

5 Since the introduction of RFL adhesion treatments for fiber reinforced rubber products, changing demands for better properties and/or new rubber products has necessitated changes in both the rubber materials and the fibers. Accordingly, cotton and rayon have been increasingly replaced by polyester fibers (polyethylene terephthalate and similar polymers) and aramid fibers {poly(p-phenylene terephthalamide) (Kevlar®), poly(m-phenylene isophthalamide), copolyterephthalamides of 3,4-diaminodiphenyl ether and p-phenylenediamine (Technora®)}. These fibers differ from the cellulosic fibers in that they have few if any groups on their surface capable of reacting with the RFL and the fiber surface is generally more crystalline and not as accessible. Modifications in the adhesive treatments have been made to overcome this problem.

15 One of the most widely used modifications constitutes pre-activation of the fiber surface, either by the fiber producer or during the adhesive treatment. Pre-activated fibers, produced by the introduction of reactive groups such as epoxides, for example, which form surface hydroxyls or other corresponding reactive groups, are commercially available. The RF portion of the RFL treatment then is thought to react with these surface groups. Another modification is to employ a two step process in the adhesive treatment of the fiber. A subcoat is first formed on the fiber surface by treatment with an epoxy or isocyanate compound or a combination of the two. This treatment can be by either a solution of the subcoat-forming compound in an organic solvent such as toluene or in an aqueous suspension of the subcoat-forming compound. Since isocyanates are so reactive with water, they are usually blocked with compounds which prevent their reaction with water at ambient temperatures and which are subsequently

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released at high temperatures to yield free isocyanate groups. The RFL treatment is then applied as a topcoat.

5 Natural and synthetic rubbers have been increasingly replaced by synthetic materials which differ structurally from natural rubber even more than the synthetic rubbers mentioned earlier. In response to the requirements of improved resistance to heat, ozone and other degrading agents, these newer elastomers generally have fewer double bonds. In addition, the double bonds that are present are usually less accessible and generally in side chains rather than in the backbone. Some examples of these materials are EPDM (Ethylene-Propylene-Diene Monomer), chlorosulfonated polyethylene (CSM or Hypalon®) and butyl (isobutylene-isoprene copolymer and halobutyl elastomers. Modifications in RFL treatments to meet these challenges have generally involved using a latex that is more compatible with the elastomer. EPDM, chlorosulfonated polyethylene and similar 10 latexes are available. Although these latexes may offer some improved adhesion over the synthetic rubber type latexes to the specific elastomer, there are still disadvantages such as expense and stability of the specialty latex and the desire for greater adhesion.

20 In addition to being less suited to the newer materials used in rubber composites and specific rubber products, RFL treatments also encounter present day environmental and safety problems. Formaldehyde presents many safety and environmental problems in the preparation of the chemical treatment, the application of the treatment, heat curing of the treatment, converting and handling of the treated yarn, and incorporation into the rubber product. Disposal of water containing the formaldehyde, resorcinol, and latex components is becoming an increasingly complex problem. 25 Lastly, due to the polymer formation on the surface of the fiber by the RF reaction, the RFL treated materials are generally stiff, more variable in regard to uniformity of concentration of the polymer along the fiber mate-

rial surface, and variable in regard to surface tackiness, causing processing problems in the incorporation of the treated materials into rubber products.

5 Isocyanates and epoxides alone and with plasticizers have been used as alternatives to RFL. These approaches generally do not give as high adhesion as RFL but they may overcome some of the environmental, safety and processing problems. In addition, a great deal of research has been directed to adhesive systems based on polyisocyanates combined with a variety of materials, one of which includes polyenes sometimes
10 terminated by groups having active hydrogens, e.g., hydroxy-terminated polybutadienes. Such systems, along with others are exemplified in the following patents.

In Japanese Patent 50087477 issued to Toshiyuki et al. in 1975, bonding of polyester fiber is said to be improved by treating the fibers with
15 a mixture of a diisocyanate prepolymer with polymer or copolymer of a mercapto-terminated halogen-containing polybutadiene derivative such as polychloroprene in a molar ratio of x:y isocyanate group to polychloroprene to give two terminal isocyanate groups plus a polyester containing at least 60% ethylene terephthalate linkages in organic solvents such as dimethyl-
20 formamide. The equivalent ratio of the isocyanate groups to the halogen-containing butadiene and hydroxyl groups from the polyester was between 0.9 and 1.3, inclusive, with the ratio of hydroxyl groups to thiol groups being between 0.5 and 2.0 inclusive.

25 East German Patent 1282913 B describes polyamide fibers bonded to a rubber mat by placing a polyethylene sheet containing a little plasticizer onto the rubber mat, coating with a solution of an isocyanate compound and rubber in an organic solvent, spreading polyamide staple fibers on top and pressing through a pair of rollers.

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Japanese Patent 49011877 issued to Shima et al. on March 20, 1974, describes poly(ethylene terephthalate) or similar polyesters modified with one or more unsaturated dicarboxylic acids, diols, or hydroxycarboxylic acids such as polybutadiene glycol, and a chain linking agent such as diphenylmethane diisocyanate dissolved in nitrobenzene for one hour at 150°C to give a material for improved dyeability of polyester fiber or improved adhesive properties of polyester tire cord.

Japanese Patent 46006358 issued to Shima et al. on February 17, 1971, describes polyester fibers and films treated with a polyester, an isocyanate and/or an epoxide, and a modified polybutadiene (molecular weight 300-10,000) that show improved adhesion to rubber and improved dyeability.

Japanese Patent 4800835 issued to Shuna et al. on March 13, 1973, describes a polyurethane adhesive for tire cords prepared from the reaction of a polyester, a carboxyl or hydroxyl group terminated polyene and a polyisocyanate containing three isocyanate groups such as toluene triisocyanate.

Henning et al. in U.S. Patent 4,870,129 issued on September 26, 1989, introduced an aqueous solution or dispersion adhesive using a polyurethane with carboxylate or sulfonate groups. The polyurethane is prepared by reacting isocyanate groups (NCO) with hydroxyl groups (OH) at a ratio range equal to 1.2 - 2.5 equivalents of NCO to 1.0 equivalents of OH.

U.S. Patent 5,045,393 issued to Kumanoya et al. on September 3, 1991, introduced a method for providing a polyolefin resin substrate with an adhesive coating using a hydroxyl hydrocarbon paint with a catalyst, which promotes the isocyanate-hydroxyl reaction, and then coating the primer film with a polyurethane prepolymer adhesive rich in isocyanate groups.

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U.S. Patent 4,552,816 issued to Spahic et al. on November 12, 1985, describes a process for producing covalently bonded laminated structures composed of polyurethane elastomer and vulcanizable rubber. The joining layer is comprised of polyurethane segments, polyisocyanate segments, and hydroxyl containing polybutadiene segments where covalent bonds exist between polyurethane and polyisocyanate segments and between the hydroxyl of the polybutadiene and the polyisocyanate segment.

U.S. Patent 3,528,878 issued to Lubowitz on September 15, 1970, describes a method for bonding rubber to fabric comprised of a polyfunctional polydiene having either hydroxyl or carboxyl groups or both, a predominant amount of vinyl groups on alternate carbon atoms of the polydiene backbone, an organic co-reacting chain extender, and a peroxide free radical initiator. A substituted diisocyanate is used as a chain extender when the polydiene contains hydroxyl groups.

Japanese Patent 01144471 issued to Iwase et al. in 1989 describes compounds containing isocyanate-modified polybutadienes having an average number molecular weight (Mn) 500-20,000, polyols having Mn 150-50,000, and acid phosphates gave good adhesion to various plastics.

U.S. Patents 3,743,616 and 3,879,248 issued to Kest on July 3, 1973, and April 22, 1975, respectively, describe a new class of and method for producing pressure sensitive adhesives for bonding to various substrates (e.g., glass, metal, paper...). The adhesive consists of a hydrocarbon polymer with at least 1.6 terminal active-hydrogen groups and an equivalent weight of 500 or greater co-reacted with an organic co-reactant having two or more reactive groups (U.S. Patent 3,743,616) or an organic polyisocyanate (U.S. Patent 3,879,248) *in situ* on the substrate web to give a pressure sensitive adhesive. In the practice of the invention, sufficient co-reactant is used to provide a ratio of 0.75-1.20 co-reactant

groups to the total of functional groups present in the diene telechelic polymer.

Japanese Patent 48022191 describes improvement in the adhesion of polyester fibers to rubbers by using a treatment comprised of a conjugated diene copolymer, having a molecular weight of 300-10,000 and 2-35 mole percent aromatic or pyridine ring and polyesters, plus polyisocyanates, polyisocyanate derivatives, or polyepoxy compounds. In addition, a curing agent or accelerator is used in the presence of isocyanate or epoxy compounds. The composition is such that the total solids present contains one gram equivalent mole of aliphatic unsaturation per 1000 molecular weight. The diene copolymer is prepared by copolymerizing a diene such as butadiene and isoprene with styrene, vinyl naphthalene, or vinyl pyridine. An application for the treated fibers is as reinforcement for tires and belts.

U.S. Patent 3,616,193 issued to Lubowitz et al. on October 26, 1971, describes polydiene resins, such as dihydroxyl terminated 1,2-polybutadiene, mixed with organic chain extenders, such as toluene diisocyanate, in the presence of a peroxide free radical initiator, such as dicumyl peroxide, to form a liquid polymeric mixture. The polydiene prepolymer is preferably reacted in equimolar proportions and strong deviations will result in a less desirable product.

European Patent 358079 issued to Lawson et al. on March 14, 1990 introduced an adhesive system useful for bonding an uncured rubber to a cured polyurethane. A fiber reinforced pad was coated with the reaction product of a hydroxyl terminated polybutadiene and toluene diisocyanate in a solvent such as toluene; dried and coated with two coats of an adhesive cement comprising of 50% diphenyl methane diisocyanate in toluene, a glycidyl diether of tetrabromobisphenol in toluene, and a 37% dispersion of p-nitrobenzene in xylene; covered with a natural tie gum; and

covered with an uncured cord-reinforced cushion stock to form an example composite pad.

5 U.S. Patent 4,091,195 issued to Vitek et al. on May 23, 1978, describes hot-melt adhesives from a number of polymers which have been at least partially cross-linked. One adhesive comprised a homogenized polybutadiene reacted with a polyisocyanate as a cross-linking agent and adding a cross-linking accelerator. No specific molar or equivalent ratios were given.

10 Japanese Patent 56136363 assigned to Mitsubishi Chemical Industries Co., Ltd. in 1981, describes a canvas fabric bonded to an EPDM (ethylene-propylene-dienemonomer) elastomer in the presence of hydrogenated hydroxyl terminated polybutadiene and diphenylmethane diisocyanate at 1.1 equivalents of isocyanate (NCO) to 1 equivalent of hydroxyl (OH).

15 Japanese Patent 47042636 issued to Shima et al. in 1972, describes polyurethane adhesives for bonding polyester fibers to rubber prepared from mixtures of polyols and a diisocyanate. Thus, polybutadiene glycol, ethylene glycol, trimethylolpropane, 2,2',4,4'-tetra(tert-butyl)-3,3'-di(hydroxyphenyl) methane, and diphenylmethane diisocyanate were
20 heated in solvent (3:7 dimethyl sulfoxide : nitrobenzene) 1.5 hours at 150°C to give a reactive copolymer solution. A 1100 denier polyethylene terephthalate fiber is immersed in the solution and heat-treated at 240°C. The fiber is mixed with natural rubber and vulcanized at 160°C with dicumyl peroxide to give a composite with adhesive strength 15.1 kg.

25 Japanese Patent 50161578, issued to Yamada et al. on December 27, 1975, describes treated non-continuous fibers with the reaction product of a hydroxyl-terminated polybutadiene with toluene diisocyanate and E-caprolactam to improve adhesion and reinforce rubber.

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5 Czechoslovakian Patent 235735 issued to Smatlove et al. on December 1, 1986, describes a method eliminating the use of solvents, discoloration of the vulcanizate, and the direct handling of toxic isocyanates. The compound is manufactured by adding to the rubber compound blend 1-25% reaction product of a hydroxyl terminated telechelic prepolymer such as an OH-terminated oligomeric polybutadiene (MW 2500) with a diisocyanate such as diphenylmethane diisocyanate at a molar ratio of OH : NCO equal to 1:(1.5-4).

10 Japanese Patent 01304168 issued to Hata on December 7, 1989, describes fibers treated with epoxides or isocyanates and then with epoxide resins and hydroxyl or carboxyl containing polybutadiene rubber before bonding and vulcanizing with organic peroxide containing rubbers for adhesion.

15 Japanese Patent 03205473 issued to Mori et al. on September 6, 1991, shows adhesives useful in bonding polyolefins in automobile interiors comprised of a main component containing a saturated hydroxyl terminated polybutadiene or their reaction products with diisocyanates and a curing component containing isocyanate terminated urethane prepolymers from hydrogenated hydroxyl terminated polybutadiene and excess polyisocyanates.

20 U.S. Patent 3,837,892 issued to Marzocchi on September 24, 1974, introduces a method for improving the bonding relationship between glass fibers and elastomeric materials. Part of the adhesive composition uses a polyurethane prepolymer containing free isocyanate groups prepared by reacting excess polyisocyanate with a hydroxyl terminated polybutadiene or similar compound at a ratio of equivalents isocyanate to
25 equivalents hydroxyl equal to at least 1.5, but preferably equal to 2.0 - 4.0.

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U.S. Patent 3,941,909 issued to Schoen et al. on March 2, 1976, introduces a process for improving the adhesive properties of ethylene-propylene copolymers and terpolymers. The surface is treated with the reaction of a rubber-like hydroxyl-containing alkadiene-derived polymer and an organic diisocyanate at a ratio of 0.9 to 1.2 equivalents of isocyanate to hydroxyl.

U.S. Patent 3,894,982 issued to Polaski on July 15, 1975 divulges adhesive compositions of a polydiene and a polyfunctional aminoorganosilane which can be utilized for bonding vulcanizable elastomers to themselves as well as other substrates. The chain extended substituted polyalkadiene reaction reacts a polybutadienediol with a diisocyanate at a slight molar excess isocyanate up to ten percent.

Japanese Patent 58217576 assigned to Sekisui Chemical Co., Ltd. in 1983, introduces urethane adhesives comprised of a hydroxyl terminated 1,2-polybutadiene ($\geq 90\%$ 1,2-units), hydroxyl terminated 1,4-polybutadiene ($\geq 60\%$ 1,4-units), polyisocyanate ($0.6 \leq \text{isocyanate/hydroxyl ratio} \leq 1.2$), aromatic or aromatic-aliphatic petroleum resin, and plasticizer. The adhesive composition is mixed, coated on a polyvinyl chloride sheet with some plasticizer, and cured to give an adhesive tape.

World Patent 92/03500 to Drake et al. on March 5, 1992, discloses adhesive rubber compounds exhibiting very strong adhesion to other elastomers, plastics and a variety of substrates. A film or spreadable liquid of this adhesive is cured in contact with the substrates to be adhered.

From the preceding description of the references, it is difficult to make any generalization except to note that the art is extraordinarily crowded with efforts to provide improved adhesives, even in a narrow area defined by the combination of, for example, isocyanates in combina-

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tion with a polymer having active hydrogen-containing end groups and double bonds.

Objects of the Invention

5 It is an object of one aspect of the present invention to provide an improved adhesion system for fibrous and related products, especially for use as reinforcing materials in composite rubber products, as well as for other uses where good adhesion is required.

An object of another aspect of the invention is to provide compositions which may be used as part of, or as the total adhesion system.

10 An object of a further aspect of the invention is to provide articles of manufacture, such as, for example, fabrics, fibers and sheets provided with the adhesion system, as well as final products such as, for example, hose, belts, tires, other mechanical rubber goods, and the like, reinforced with the treated articles of this invention.

15 Upon further study of the specification and appended claims, further objects and advantages of aspects of this invention will become apparent to those skilled in the art.

Summary of the Invention

20 These and other objects are achieved through the adhesive system of the present invention which comprise(s): (a) an isocyanate compound, (b) one or more of a polyunsaturated polymer (or oligomer), hereinafter referred to as "hydrocarbon polymer", where the backbone of such a polymer comprises carbon-carbon bonds and which contains some carbon-carbon double bonds or groups capable of forming some carbon-carbon double bonds or otherwise can undergo free radical reaction and/or a
25 polyunsaturated polymer (or oligomer), hereinafter referred to as a "heteroatom polymer", which has a heteroatom backbone, that is, the

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polymer backbone contains atoms other than, and bonded to, carbon, such as oxygen, nitrogen and sulfur, which also contains unsaturated groups as for the hydrocarbon polymer. Both of these types of polyunsaturated polymers may contain active hydrogen functional groups which can react with or have reacted with an isocyanate compound. These reactive groups are usually terminal end groups, but they can also be along the polymer backbone or off of side chains, and (c) a carrier for dissolving or dispersing (a) and (b) and optionally other functions, especially when a plasticizer is used as a carrier. Each of these components contributes, either singularly or in combination with other components to achieving the advantages of the invention. This adhesion system can be applied to filament yarns, fabrics and other fibrous materials and other products such as films and sheets to impart improved adhesion of these articles to rubbers and synthetic elastomers and other unsaturated polymeric products which are difficult to bond with existing treatments. In general, the adhesion system can be used to join any type or form of material to another material, whether it be the same or different.

The components of this invention either form a homogeneous solution or uniform dispersion which can be applied to the articles without the use of emissive solvents and without pretreatments or separate treatments and without adversely affecting the articles in their processing and use with the rubber materials or other unsaturated polymeric materials containing carbon-carbon double bonds.

Isocyanate compounds are an essential part of this invention. These compounds, which generally should contain two or more isocyanate groups per molecule, apparently contribute to the adhesion improvements of this invention in more than one way. Some of these isocyanate molecules may react with the polyunsaturated polymers which are the second component of this adhesion system. However, it has been surprisingly

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found that additional isocyanate compound, other than that which reacts with the polyunsaturated polymer component, is necessary. Therefore, very large molar ratios of the isocyanate compound to the polyunsaturated polymers, which results in a large excess of isocyanate groups over what
5 can react with the polyunsaturated polymer, are unexpectedly required in order to obtain the adhesion improvements imparted by the adhesion system of this invention.

The molar ratio is calculated as the number of moles of isocyanate groups to the number of moles of functional groups on the polyunsaturated
10 polymer capable of reacting with the isocyanate. The specific molar ratio used may be dependent on the hydrocarbon polymer and/or heteroatom polymer used, the monomers used to form the polymer(s), the type of reactive groups in the polymer(s), the number of unsaturated groups in the polymer(s) and the amount and type of isocyanate used, among other
15 things. However, at least about 1.5 times molar excess of isocyanate has been found necessary to impart the improved adhesion of this invention in the case of the hydrocarbon polymers with ratios such as 200 to 1 and higher giving very significant adhesion improvements. The heteroatom polymers generally give adhesion improvement at even higher molar ratios
20 than the hydrocarbon polymers. The combination of a hydrocarbon polymer and a heteroatom polymer also allows higher molar ratios of isocyanate groups of each polymer than with either polymer alone.

Specifically, the preferred adhesion system comprises excess polyisocyanate molecules plus polyisocyanate reacted with isocyanate
25 reactive polyunsaturated compounds plus plasticizers.

The isocyanate compounds of this invention include, but are not limited to, those defined by D.H. Chadwick and T.H. Cleveland in "Isocyanates, Organic", *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 13, pp. 789-818, Martin Grayson - Editor, John Wiley &

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Sons, New York, 1981. Preferred isocyanate compounds of this invention include compounds which contain at least two isocyanate groups and/or isocyanate equivalent groups. Preferred compounds include diisocyanates, polyisocyanates, prepolymers containing urethane or amide linkages with free isocyanate groups and dimers, trimers, oligomers and copolymers of isocyanates, such as those obtained from diisocyanates. Compounds with isocyanate equivalent groups include those which have their isocyanate groups blocked with a potentially fugitive blocking agent, adducts and derivatives of compounds having isocyanate groups with other reactive species such as biurets or isocyanurates, and compounds which may not contain isocyanate groups or their derivatives but do contain groups which react like isocyanates such as, for example, carbodiimides and compounds which contain isothiocyanate groups.

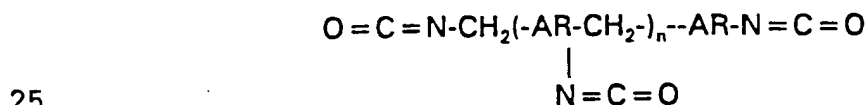
Representative species suitable for use as at least one of the isocyanate compounds in this invention include but are not limited to toluene diisocyanate (TDI) (2,4 and 2,6-isomers and mixtures), hexamethylene diisocyanate (HDI), meta-tetramethylxylylene diisocyanate, bis(4-isocyanatocyclohexyl)methane (hydrogenated MDI), (1,4-bis(isocyanatomethyl) cyclohexane, isophorone diisocyanate (IPDI), diphenylmethane 4,4'-diisocyanate (MDI), polymeric or oligomeric MDI or polymethylene polyphenyl isocyanate (either 2,4' or 4,4'-isomers or any mixture of these), p-xylylene diisocyanate, toluene triisocyanate, the biuret of hexamethylene diisocyanate, the adduct of TDI with trimethylol propane, the trimer (isocyanurate ring) of TDI, HDI or a copolymer of the two; the dimer of TDI; caprolactam, phenol, substituted phenol, butanone oxime or similar oxime blocked TDI, HDI or other isocyanate or derivative as described above, polycarbodiimide modified MDI and other isocyanates and polyureas of TDI, 1,4-benzene diisocyanate, dianisidine diisocyanate, 1-chlorophenyl-2,4-diisocyanate, trimethylene diisocyanate, pentamethy-

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lene diisocyanate, butylene-1,2-diisocyanate, butylene-1,4-diisocyanate, xylene diisocyanate, 2,4-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, 1,1-dibutylether diisocyanate, 1,6-cyclopentane diisocyanate, 2,5-indene diisocyanate, 1,5-naphthalene diisocyanate, triphenylmethane diisocyanate, 1,12-diisocyanatododecane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane, 4,4'-diisocyanatodicyclohexylpropane-(2,2) and other di or polyisocyanates containing free isocyanate groups.

The isocyanate compounds defined above may be mixed with compounds that contain one isocyanate group which include, but are not limited to dimethyl meta-isopropenyl benzyl isocyanate, hexyl isocyanate, ortho, para or meta-tolyl isocyanate, 1,4-phenylene isocyanate, 1,4-phenyleneisothiocyanate, 4-methoxyphenylisocyanate, 4-methoxyphenyl isothiocyanate, p-cyanophenyl isocyanate.

Isocyanate compounds which contain two or more isocyanate groups are preferred in this invention. The polymethylene polyphenyl isocyanates or polymeric MDI, which are oligomers or polymers of MDI, are particularly preferred. Polymethylene polyphenyl isocyanate (PMPPI) is available from a number of sources such as BASF Corporation, Dow Chemical USA and Miles Inc. (formerly Mobay) and several others. These products are a mixture of the various possibilities which can be represented by the following formula, giving five different compounds in terms of "n" in that formula and two major isomers, 2,4' and 4,4'.



Where AR is a phenyl group and $n = 0$ to 4.

These mixtures, which generally contain about 50% $n = 0$ product (MDI), have an isocyanate functionality ranging from greater than 2.0 to about 3.0 or higher ($\text{MDI} = 2.0$) and have an isocyanate content of about 30 to about 33%. Reactive group functionality, such as isocyanate func-

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tionality, refers to the average number of reactive groups per molecule or moles reactive groups/mole of compound. Even though these compounds contain more than two isocyanate groups, they surprisingly do not form excessive crosslinks or insoluble materials, even when mixed with other reactive components of this invention within a carrier. For example, the Desmodur series of Miles Inc. varies according to the following Table:

	DESMODUR TYPE	TYPICAL PERCENT ISOCYANATE	TYPICAL FUNCTIONALITY	TYPICAL VISCOSITY	ISOMER
10	VKS-2	33		20	65% 4,4' & 35% 2,4'
	VKS-4	32.5	2.4	40	65% 4,4' & 35% 2,4'
15	VKS-5	32.4		57	65% 4,4' & 35% 2,4'
	VKS-18	31	2.75	180	65% 4,4' & 35% 2,4'
	VK-5	32.5	2.3	50	95% 4,4' & 5% 2,4'
20	VK-18	31.5	2.7	180	95% 4,4' & 5% 2,4'
	VK-70	31	2.8	700	95% 4,4' & 5% 2,4'
25	VK-200	30.6	3.0-3.3	2000	95% 4,4' & 5% 2,4'

Although all of the polymethylene polyphenyl isocyanates will yield improved adhesion in this invention, the Desmodur VKS-18 and Desmodur VK-18 polymethylene polyphenyl isocyanates are preferred for their balance of adhesion improvement and treating solution stability. Not wishing to be bound by theory, with all other characteristics being equal, the increased branching of the 2,4'-isomer appears to offer better treating solution stability and better processing.

The second component of this invention comprises one or more of a polymer and/or oligomer which contains more than one unsaturated

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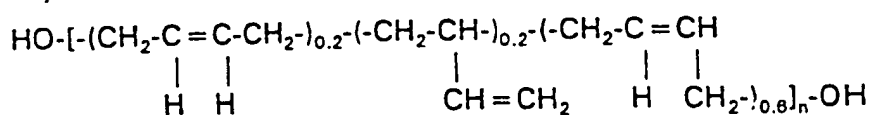
group or carbon-to-carbon double bond unit either in the backbone or as side chains or other groups capable of forming unsaturated groups or otherwise undergoing free radical reaction or other such reaction to cross-link or otherwise react with rubber and other polymer molecules during rubber vulcanization or similar processes, such as but not limited to chlorosulfonated polyethylene, which may lose SO₂ during vulcanization or cure to develop unsaturated groups (Paul R. Johnson, p. 787 in *Martin Grayson/Executive Editor, Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 8, Wiley-Interscience, New York) and similar polymers as described in Volume 8. The polyunsaturated polymer generally has at least one active hydrogen functional group per molecule, generally as a terminal group but possibly along the polymer chain or attached to side chains, such as hydroxyl, carboxyl, amine, thiol, hydroxyl amine and other active hydrogen functional groups which may react with the isocyanate groups in the treating solution and/or on the treated article. These polyunsaturated polymers may be either (a) the hydrocarbon polymers, usually made by a free radical chain polymerization (addition polymerization) or (b) the heteroatom polymers, usually made by condensation or step-reaction polymerization.

Typical of the first type of polymers or hydrocarbon polymers, which can have atoms other than hydrogen connected to the carbon atoms in the polymer backbone, are homopolymers or copolymers of polyene or diene monomers including but not limited to butadiene, isoprene, chloroprene, 2,3-dimethylbutadiene, 2,4-hexadiene, ethylidene norbornene, 1,4-hexadiene, dicyclopentadiene, cyclopentene and the like, which upon polymerization leave a double bond or unsaturated group in the chain or as side chain. The copolymers include copolymers of the diene monomers with each other or vinyl monomers such as isobutylene, ethylene, propylene, butene, vinyl ethers and the like, with vinyl substituted aro-

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matic compounds such as, for example, styrene, vinyl toluene, vinyl pyridine, or with acrylic monomers such as, for example, acrylonitrile, acrylic and methacrylic acids, amides and esters or with any other unsaturated monomers capable of polymerizing with the polyenes or dienes.

5 The hydrocarbon polymers of this invention typically should have at least one and preferably on the average at least about three or five and more preferably about 10 repeat units or carbon-carbon double bond units capable of undergoing free radical addition. The limiting factor on the high side of repeat units of the diene monomers, and any comonomers included, is to preferably maintain the hydrocarbon polymer in a liquid state or to maintain solubility or dispersibility of the hydrocarbon polymer in the other components of this invention. Corresponding molecular weight values for these degree of polymerization ranges would depend on comonomers included in the polymer. A preferred range of average degree of polymerization is from about 10 to about 100. An even more preferred average degree of polymerization is about 15 to about 75 and especially about 30-50, which is represented in polybutadiene Poly bd[®] R45HT, a commercial product from Atochem North America, Inc. (Poly bd[®] is a trademark of Atochem North America). This commercial polymer is a liquid, hydroxyl-terminated homopolymer of butadiene with a number average molecular weight of about 2800, polydispersity (Mw/Mn) of 2.5 (so Mw = 7000), a viscosity of about 5000 mPa·s at 30°C, a specific gravity of about 0.901 at 30°C and an iodine number of about 400 and glass transition temperature (T_g) of -75°C. The predominant configuration of this polymer is about 60% trans, 20% cis and 20% vinyl as represented by the following formula:



where n = 50.

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The hydroxyl value of this preferred hydrocarbon polymer is about 0.86 meq/g with a hydroxyl number of about 48.2 mg KOH/g, representing a hydroxyl functionality in the range of 2.4 to 2.6. Another preferred hydroxyl-terminated hydrocarbon polymer is Poly bd R20LM from Atochem. This polymer has a degree of polymerization of about 25, a number average molecular weight of about 1230, with a polydispersity value (Mw/Mn) of 2.0, a viscosity of about 2600 mPa·s at 23°C, a hydroxyl value of about 1.8 meq/g, representing a hydroxyl functionality in the range of 2.4-2.6 glass transition temperature (Tg) of approximately 2.5.

Terminal or other groups in the hydrocarbon polymer which can react with the isocyanate component of this invention, other than hydroxyl groups, include but are not limited to carboxylic acid, thiol, amine, as well as other groups which will react with isocyanate groups. One example of a polymer with carboxyl groups along the chain is the adducts of, for example, maleic anhydride with polybutadiene and other polymers as described by Drake and Labriola in WO 92/03500.

Amine terminal groups are generally more reactive than hydroxyl-terminal groups and can, in some cases, give more insoluble products and, in such cases, can be combined with selected plasticizers and other components of this invention to give usable treating solutions.

Although a reactive group functionality of around 1.0 to 3.0 functional groups per polymer molecule is preferred and about 1.9 to about 2.6 functional groups per polymer molecule is more preferred, the improved adhesion of this invention should be obtained with polymers having a reactive group functionality of as low as 0.1 or even lower, or higher than 3.0, with the selection of the proper components of this invention. In fact, some of the hydroxyl groups of these hydrocarbon polymers, such as Poly bd R45HT, can be reacted so that non-isocyanate reactive groups,

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such as, for example, acrylate, vinyl, phenyl, alkyl and the like, are present. In the case of where the functionality is below one, some polymer molecules may not react with the isocyanate groups, but they still may contribute to adhesion improvements by physical entanglements or other mechanisms. In the case of functionalities significantly below 1.0, the actual molar ratio of NCO to actual reactive group will increase significantly and may even approach infinity.

Some of the double bonds of the hydrocarbon polymers of this invention can be further reacted either before or after the polymer's reaction with isocyanate, such as being epoxidized or oxidized, for example. Representative of such polymers include but are not limited to Poly bd 600 and 605 Resins from Atochem North America.

It has also been discovered that phenyl terminated polybutadiene combined with the isocyanate compound and plasticizer has yielded good adhesion. In such a case, where phenyl or other non-reactive hydrocarbon functional group is used, some reactive groups may have been introduced in some manner and the molar ratio of isocyanate groups to active hydrogen groups will exceed 200:1 may even greatly exceed 200:1 and may even approach infinity. Without wishing to be bound by an explanation, the phenyl-terminated polybutadienes employed in the examples may have had hydroxyl groups since they were subject to atmospheric conditions for several years without the protection of antioxidants.

Typical of the heteroatom polymers of this invention are unsaturated polyesters, polyamides, polyurethanes, and polyethers, where either at least one of the difunctional dicarboxylic acids, isocyanates, epoxides or methylol condensates and/or at least one of the difunctional alcohols, thiols or amines involved in the polymerization reaction have double bonds or unsaturated groups. These polymers will usually have active hydrogen groups, which will react with the isocyanate compounds of this invention,

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as terminal groups and even as side groups, if polyfunctional monomers are used. The nature of these terminal reactive groups will be dependent on the molar ratio and of the two reactants whether the active hydrogen groups were hydroxyl, amine or thiol or a combination thereof.

5 The polyester and polyamide polymers can be made by reacting unsaturated dicarboxylic acids, or their derivatives such as, for example, anhydrides, esters, acid chlorides, amic acids, amides and the like with diols, in the case of polyesters, and with diamines, in the case of polyamides. The dicarboxylic acids can be aromatic as well as aliphatic,
10 and they preferably have at least one double bond, preferably a carbon to carbon unconjugated double bond.

 Examples of dicarboxylic acids, and their derivatives as described above, for heteroatom polymers of this invention include but are not limited to maleic, itaconic, citraconic, fumaric, trans-3-hexene-dioic
15 acids, anhydrides and acid chlorides; 1-cyclopentene-1,2-dicarboxylic anhydride; alkenyl substituted succinic anhydrides and the like. These unsaturated dicarboxylic acids can be mixed with saturated or other dicarboxylic acids which do not undergo free radical addition, such as, for example, succinic, phthalic, terephthalic, trimellitic acid and similar acids
20 as long as there are enough reactive double bonds in the resulting polymer to give the desired adhesion. The same applies to unsaturated or saturated acids having more than two carboxyl groups as long as the solubility or dispersibility in the other components of this invention is maintained. Either the saturated or unsaturated dicarboxylic acids or their derivatives
25 or a mixture of the two can be reacted with unsaturated polyols and/or polyamines.

 The heteroatom polymers of this invention can vary widely in regard to average degree of polymerization or number of repeat units of unsaturated units. The upper limit will generally be dictated by the desire to

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maintain a liquid state or solubility in plasticizers or solvents, but preferably will be about 30 repeat units and more preferably about 20 repeat units. The lower limit should be more than one repeat unit of unsaturated units and preferably at least three or five repeat units and more preferably at least eight repeat units.

5 The polyhydroxy compounds should contain at least two hydroxyl groups, with the preferred group being diols. Particularly preferred diols are sterically hindered 2,2,4-tri(lower)alkyl pentane-1,3-diols, especially 2,2,4-tri-(C₁-C₃)-alkylpentane-1,3-diol, although other diols, even those
10 containing other functional groups or aromatic hydrocarbon components or further reacted additional hydroxyl groups, should be suitable in the polyunsaturated polycarboxyls of this invention. Representative diols, both saturated and unsaturated, include but are not limited to: 2,2,4-trimethyl-1,3-pentanediol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol,
15 2,4-dimethyl-2-ethyl-1,3-hexanediol, 1,6-hexanediol, 1,5-hexanediol, 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, hydroxyl-terminated butadiene, isoprene, chloroprene and the like homopolymers and copolymers, 7-octene-1,2-diol, 5-norbornene-2,2-dimethanol, cis-3,5-cyclohexadiene-1,2-diol, ethylene glycol, propylene glycol,
20 diethylene glycol, polyethylene glycol, polypropylene glycol, 2,2'-thiodiethanol, 1,3-propane diol, 2-methyl-1,3-propane diol, resorcinol, 1,3-dihydroxynaphthalene, cyclohexane dimethanol, 3-allyloxy-1,2-propanediol, 2-amino-2-ethyl-1,3-propanediol, 2,3-dihydroxypropylacrylate and methacrylate, N,N'-(1,2-dihydroxyethylene)bisacrylamide,
25 dihydroxycinnamic acid, 2,4-dihydroxybenzoic acid dihydroxyfumaric acid and similar diols and combinations of any of these diols. Triols and higher, such as glycerol, trimethylol propane and pentaerythritol can be used, but crosslinking and insolubilization may result, so blends of polyols with diols may be useful. Polyamines, such as 1,6-diaminohexane, p-phenylene-

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5 diamine, 1,3-pentanediamine, 2-methylpentamethylenediamine, 1,2-diaminocyclohexane and 1,2-diamino-2-methylpropane, amine terminated butadiene, isoprene, chloroprene and the like homopolymers and copolymers, and disulfides, such as 1,6-hexanedithiol, dithioerythritol, 1,4-butanedithiol, 2,3-butanedithiol, thiol terminated butadiene, isoprene, chloroprene homopolymers and copolymers and the like can also be used to give polyamides or polythiol esters. Combinations of polyols, polyamines and polythiols or even compounds containing combinations of these functional groups on the same molecule, as well as other functional groups such as carboxylic acids, can also be used. Mixed group compounds, such as ethanol amine, 2-mercaptoethanol, 3-amino-1-propanol, 6-amino-1-hexanol, 2-(2-aminoethoxy)ethanol and 2-(2-aminoethylamino)-ethanol, can also be used to give, for example, a polymer containing both amide and ester groups.

15 Other heteroatom polymers contemplated by this invention are polymers formed by the reaction of polyreactive compounds other than polycarboxylic acids and their derivatives with the active hydrogen containing compounds as described above. Examples of such polyreactive compounds include, but are not limited to polyisocyanates, as defined under component a) of this invention, polyepoxides, such as ethylene and polyethylene glycol diglycidyl ether, propylene and propylene glycol diglycidyl ether, resorcinol diglycidyl ether, neopentyl glycol diglycidyl ether, the glycidyl ester ether of p-hydroxy benzoic acid, 1,6-hexanediol diglycidyl ether, bisphenol A diglycidyl ether, allyl glycidyl ether, o-phthalic acid diglycidyl ester, terephthalic acid diglycidyl ester, hydroquinone diglycidyl ester, an unsaturated high molecular weight dicarboxylic acid diglycidyl ester sold as Denacol EX-1114 from Nagase Chemicals, Ltd., dibromo neopentyl glycol diglycidyl ether, glycerol polyglycidyl ether, trimethylolpropane polyglycidyl ether and other similar compounds, and polymethylol

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compounds and their derivatives, such as methyolated methylated and other alkylated methylol melamines, ureas, cyclic ureas, phenols, and resorcinol and other such polyfunctional compounds capable of reacting with active hydrogen groups.

5 In the adhesion system of this invention, some of the isocyanate compound of component a) presumably reacts with the reactive groups of the polyunsaturated polymer component. This reaction product, which is also a component of the adhesion system of this invention, is preferably formed *in situ* in the treating solution and/or on the treated article by
10 adding the large excess of isocyanate compound to the polyunsaturated polymer or polymers and the carrier component and then applying this mixture to the treated article. However, this reaction product can be formed separately and added to the additional isocyanate component and carrier and even additional polyunsaturated polymer of either type if advantageous. This can be done for either type of polyunsaturated polymer, either
15 alone or together.

Especially surprising is the fact that a combination of the two types of polyunsaturated polymers, i.e., the hydrocarbon polymers and the heteroatom polymers, gives better adhesion in most cases than either
20 polymer alone. Indeed, the combination of these two types of polymers, particularly polybutadiene diol and poly(2,2,4-trimethyl-1,3-diol maleate), in combination with the polyisocyanates and plasticizers of this invention appear to be preferred.

The third component of this invention is the carrier, which can perform several functions for the adhesion system of this invention. One
25 function is to serve as a solvent for dispersing or solubilizing the other two components and for other plasticizers or other additives. Indeed, ordinary solvents such as, for example, toluene, xylene and other aromatic hydrocarbons, ketones, e.g., acetone, methyl ethyl ketone and methyl iso-

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butyl ketone, esters, e.g., ethyl acetate and butyl acetate; tetrahydrofuran (THF) and other ethers, mineral spirits, 1,1,1-trichloroethane and other chlorinated and chlorofluorinated and fluorinated solvents, 2-(1-methoxy)propyl acetate, nitrobenzene, nitriles, such as acetonitrile, adiponitrile and pentenenitrile, dimethyl formamide, dimethyl sulfoxide, N-methyl pyrrolidone, alkanes, hexane, mineral oil, paraffin oil, naphthenic oil, sulfonated oils and similar oils, mono- and polyglycols and their mono- and di-esters and ethers and related materials and combinations of any of the above can be used as a carrier, either alone or in combination with each other or with plasticizers, to impart improved adhesion to the treated material. Water can also serve as a carrier if the other components of this invention are emulsified or dispersed in it. The isocyanate may also have to be blocked to prevent premature reaction with water, depending on the time and application methods involved.

It is, however, generally preferred to use a plasticizer as a carrier because it can also perform other functions, as well as generally impart better adhesion with the other two components than a solvent functioning as a carrier. In addition to functioning as a solvent or a dispersing agent and a viscosity modifier, the plasticizer or plasticizer combination can affect the surface of the material to be treated so that the isocyanate compounds and any polymer forming from them, either by reaction with the polyunsaturated polymer or with water or both, may be able to better penetrate the surface of the material to be treated and become better attached to it, either physically by molecular entanglement, and/or chemically by making more reactive end groups of the material to be treated accessible. The plasticizer, by nature of its general hydrophobicity, can also function to protect the isocyanate groups so that they do not react with water either in the air, in solution or on the treated article, as rapidly. The plasticizer or plasticizer combinations can also affect the surface of the rubber

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where it contacts the fibrous material or related article by softening, swelling or other mechanism, to make a more physically compatible interface to facilitate any chemical reactions between the rubber and chemically treated fibrous material surface.

5 Another important function of the plasticizer can be to modify the surface of the treated filament yarns or fibrous materials for processing. For example, the higher alkyl adipate and phthalate esters can impart softness and lubricity to the treated article while more hydrophilic esters, particularly phosphates, can impart antistatic properties. Finally, a very
10 significant advantage of the plasticizer is that it, or a combination of plasticizers can perform all of the above functions, including acting as a carrier for the isocyanate and unsaturated oligomer or polymers and any reaction products thereof without having to be disposed of or reclaimed as a solvent, either aqueous or nonaqueous, would have to be. The plastici-
15 zer(s) stays with the treated material and then with the rubber material once it is formed. This feature saves energy from eliminating the need to remove a solvent from the treated material and possibly recovering and/or purifying the solvent and eliminates environmental contamination by release of a solvent to the atmosphere during removal or recovery or upon
20 disposal of a solvent which cannot be recovered.

 These plasticizers should be liquid, soluble or dispersible in other components of the mixture, or soluble or dispersible in a solvent that is compatible with the other components. Liquid plasticizers which can help solubilize other components of the mixture are particularly preferred.

25 Plasticizers constitute a broad class of chemical compounds. A chemical is generally classified as a plasticizer if it modifies the physical properties of a plastic or related material, including rubber or synthetic elastomers. This modification of the physical properties is again quite broad and includes a variety of uses such as modification to change vis-

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cosity, flexibility, strength, improve the workability during fabrication and even extend the natural properties of the plastic or rubber. Plasticizers are routinely added to rubber compounds to modify their properties. Such broad classes as organic and inorganic esters and amides (mono and poly-carboxylic acids, phosphoric acid, sulfuric and sulfonic acid and other acids, alkyl and aromatic), hydrocarbons and halogenated, epoxidized and other modified esters and hydrocarbons encompass plasticizers. If a compound does not fall into the broad chemical class just described and still modifies the physical properties of a plastic or rubber material, it functions as a plasticizer. Also, one class of chemicals may function well as a plasticizer for certain plastics or rubbers, but may have little or no effect on the properties of other plastics or rubbers. For example, various silicones may be excellent as plasticizers for silicone polymers and rubbers but may have no plasticizing effect on more hydrophilic rubbers and plastics.

A chemical is classified as a plasticizer for the purpose of this invention if it is classified as a plasticizer by the general definition above, in the general chemical literature or by the technical literature or advertisements of a supplier, if it is conventionally known as a plasticizer or if it has swelling, softening or other effect on the physical properties of the fiber or other material to be treated or the rubber or other polymeric material to be adhered to.

In regard to choosing plasticizers for the adhesive system of this invention, the effect of the plasticizer on the particular rubber and fiber, which structurally is a combination of plastic and rubber domains or regions, or similar material to be treated and bonded is thought to play a significant role. However, other factors, such as the ability to dissolve the other components, both as added to the treating formulation and as may be formed *in situ*, either by reacting with each other or with other species such as water in the air, its viscosity, its volatility and its effect

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on processing of the treated fibrous or related material in its incorporation or preparation for incorporation into the particular composite structure and other effects are also thought to be important. It has been found that combinations of two or more plasticizers can be quite beneficial in the formulations of this invention. These plasticizers may modify the different rubber and plastic materials in different ways and/or may contribute in some or all of the other factors described above. Particularly preferred plasticizers are the common alkyl esters of adipic, phthalic and terephthalic, sebacic, azelaic, glutaric, oleic, pelargonic, lauric and similar acids. Even more preferred are straight and branched chain dioctyl adipate, dioctyl terephthalate, dioctyl phthalate and alkyl mixtures and variations of these compounds, such as, but not limited to di(2-ethylhexyl) adipate, di(2-ethylhexyl) phthalate, di(2-ethylhexyl) terephthalate, di(n-octyl) adipate, di(n-octyl) phthalate, di(n-octyl) terephthalate, di(isooctyl) adipate, di(isooctyl) phthalate, di(isooctyl) terephthalate, di(C₇₋₁₁-alkyl) adipate, di(C₇₋₁₁-alkyl) phthalate, di(C₇₋₁₁-alkyl) terephthalate, diisobutyl adipate, mixed C₄₋₁₁-alkyl phthalates, diundecyl phthalate, dinonyl adipate, di(n-decyl adipate), (n-decyl, n-octyl) adipate, and (2-ethylhexyl, n-octyl) adipate. Specialty plasticizers, such as phosphate esters (tributoxyethyl phosphate, tricresyl phosphate and the like), dibutoxyethyl phthalate, N-n-butylbenzene sulfonamide, and the like, can be mixed with these basic plasticizers to enhance solubility, viscosity and specific properties of the treated article and the rubber product. Plasticizers with reactive groups, such as but not limited to dibutyl maleate, dioctyl maleate, polyethylene glycol monopelargonate, polyethylene glycol mono- and dioleate, and tri-alkyl citrates can also be used and may offer certain advantages.

The polyunsaturated polymers of this invention do not impart any significant adhesion when applied to the article alone in solvent or with plasticizer. Some adhesion, depending on the particular elastomer and

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other components of the rubber compound can be imparted by application of the isocyanate alone to the article. Generally, even more adhesion can be imparted by applying the polyisocyanate in conjunction with a plasticizer or combination of plasticizers. The magnitude of the adhesion can be varied by the choices of plasticizer and to some extent the polyisocyanate, and is also quite dependent on the type of rubber compound. In general, the combination of isocyanates and plasticizers may give significant adhesion improvements in regard to natural and the older synthetic rubbers, but the adhesion system of this invention will give improved adhesion to these rubbers as well as the newer more difficult to bond to synthetic elastomers such as EPDM, chlorosulfonated polyethylene (CPM) and butyls.

Not wishing to be bound by theory, the isocyanate compounds, the polyunsaturated polymers and plasticizers of this adhesive system probably perform a number of functions in affecting the improved adhesion to rubber compounds. Each of these components contributes, either singularly or in combination with other components, to achieving the advantages of the invention. For example, in regard to the isocyanate compounds and the polyunsaturated polymers, the isocyanate groups cannot only react with the terminal or other reactive groups of the unsaturated oligomers and polymers, reactive groups on the fiber or related material surface and possibly even reactive groups in the matrix rubber compound but also with water in the atmosphere. The reaction of water with an isocyanate group gives an unstable acid ($R-NH-C(O)-OH$) which loses carbon dioxide to give an amine end group ($R-NH_2 + CO_2$). This amine group can then react with other isocyanate groups to form amide linkages which can form polyamides on the fiber or related article surface. These polyamides can make the surface of the fiber or related material more uniform by filling in cavities, giving better physical interaction and contact with the

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rubber surface so that better bonding can take place. At the same time, this forming polyamide is and has interacted with the polyunsaturated polymer, certainly physically and even chemically if the polyunsaturated polymer has reactive terminal or side groups that can react with the isocyanate groups of the forming polyamides. The plasticizers can facilitate this activity by physically interacting with the polymer molecules of the fiber or similar article, particularly on the surface, to make them more accessible. By forming such a matrix on the surface of the fiber or related material, the double bonds of the polyunsaturated polymer may be in a better position to interact with the double bonds of the rubber or synthetic elastomer material, particularly with those less accessible double bonds such as in EPDM, during the vulcanization process.

In the vulcanization process, double bonds of the rubber or synthetic elastomer are connected with each other by a free radical mechanism using sulfur or sulfur compounds or peroxides or other materials so that a crosslinked, less liquid and elastic material is formed. See *Vulcanization of Elastomers*, Ed. G. Aleger and I.J. Sjothun, Rinehold Pub. Co. (1964). Not wishing to be bound by theory, it is believed that by using the unique combinations of this invention, the double bonds of the polyunsaturated polymer can participate in this crosslinking reaction, bonding the surface of the treated fibrous material or related article to the rubber. These double bonds can be made more accessible by the action of the plasticizers on the fiber surface and particularly the rubber, particularly under the heat conditions of the vulcanization process, to make the unsaturated groups from the rubber and fiber more accessible to each other. This result can not only give the greatly improved adhesion values shown in the following examples but can also give better adhesion to meet the ever increasing demands modern technology places on rubber products in regard to retention of adhesion upon exposure to very high tempera-

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tures, dynamic adhesion where the rubber product is exposed to continuous flexing and other mechanical stress which can otherwise break any physical adhesion between the fibrous material or related article to the matrix rubber.

5 The above reasoning may explain the very surprising result that little improvement in adhesion is obtained if the ratio of isocyanate groups to reactive groups of the polyunsaturated polymer is low so that the amount of free isocyanate compound present on the surface of the treated fibrous material or related product is very low. If one considers that the
10 accessibility of the double bonds may be different in the two different types of polymers used in this invention, the above reasoning may also explain the other surprising result that the use of two different types of polyunsaturated polymer can give better adhesion than just one.

 The present invention provides significant flexibility to a chemist in
15 the field in tailoring the adhesion needed to meet the rigorous demands imposed on rubber products now and in the future. The teachings of the chemical choices of the present invention can be used to obtain optimum adhesion by routine experimentation by consideration of the article to be treated and the formulation of the rubber compound in terms of rubber
20 polymer or synthetic elastomer type and amount; filler type and amount; accelerator type and amount; and other additives.

 Although the treated fibrous materials and related materials of the invention give their best performance in imparting greatly improved adhesion to EPDM and other difficult to adhere to rubbers, they generally give
25 improved adhesion to any given rubber compound, without changing any of the variables in the compounding formulation. Such changes, although they may enhance the adhesion, may not be possible because the variables of the rubber compound formulation may be set by the end use demands of the rubber product. Such changes are generally not necessary

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for the materials of the invention to impart their improved adhesion and other benefits. However, if one does have flexibility in changing some of the variables in the compound formulation, the adhesive systems of the present invention are believed to generally give their best adhesion performance with higher concentrations of rubber polymer and accelerator in the matrix.

In particular, the adhesion system of this invention works especially well with rubber compounds and materials which are very difficult to bond with the conventional adhesive treatments. For example, rubber compounds filled with carbon can be more difficult to obtain good adhesion to reinforcements than with rubber compounds filled with minerals and clay. Reinforcement materials treated with the adhesive system of this invention give significantly improved adhesion to rubber compounds filled with carbon.

A wide variety of materials may be treated with the adhesive system of the invention by any of the common methods of application of chemicals to that particular article. One of the most preferred applications of the adhesive system of this invention is to treat filament yarns used as reinforcement particularly in hose, but also in conveyor belts, drive belts, tires, molded articles, and other mechanical rubber goods. The adhesive system of this invention can be applied to the yarns by a variety of techniques but are most preferably applied by a kiss roll technique where a roll is rotated in a solution to be applied and becomes coated continuously with that solution. The filaments are then passed over the surface of the kiss roll, at different angles and speeds to control the amount of solution applied, to pick up the solution from the roll and to be wound onto a new package. Another preferred technique is to use a metering pump to pump the solution through a tube, at a precise rate controlled by the metering pump, to an applicator such as a slot, where the yarn runs through, with

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a hole in the slot to allow the liquid to be absorbed by the yarn as it moves through.

5 If no solvent is included in the adhesive system, the yarn does not have to be dried to remove the solvent. Also, the treated yarn does not have to undergo extensive and high temperature heat treatments to cause the treatment to be effective. In fact, the treated yarn, immediately after treatment, can be wound onto tubes for further processing for their intended use. These tubes may be given a heat treatment by placing them in an oven for a particular time and temperature, preferably at about 10 200°F for about 3 to 4 hours. This heat treatment may allow the chemicals to better penetrate the surface of the yarn to give better processing and less removal of the treatment chemicals as the yarn passes over various surfaces in subsequent unwinding and winding operations and as the yarn passes over various surfaces in its incorporation into hoses and 15 other mechanical rubber goods.

In many situations, however, no heat treatment is required to effect improved adhesion, as particularly shown in Example 70. This ease of treatment gives the materials of this invention especially significant advantages over conventional RFL treatments which must be, in the case of a pretreatment with isocyanate, dried or cured at temperatures generally 20 over 400°F and dried again to remove water from the RFL treatment and must be cured at temperatures generally above 350°F to effect the reactions of the resorcinol with formaldehyde and that product with the latex and the fiber.

25 Also, RFL treated yarns, probably because of their water solvent, must be dried before winding onto tubes. If RFL treated yarns were wound directly onto tubes and then dried, the resulting yarn would be very sticky and very difficult, if not almost impossible, to unwind and would be very uneven in regard to amount of material on the yarn. In fact,

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uneven treatment, due to a combination of factors including uneven drying and uneven reaction along the yarn, is common with RFL treatments, adversely affecting processing of the yarn into hose or other product incorporation steps and resulting in variable adhesion. Furthermore, conventional RFL treated yarns are generally stiff, probably due to the extensive polymer formation on the surface of the yarn. On the other hand, the treated yarns of this invention can be varied as required to be stiff, soft or intermediate, depending on the choice of plasticizers in the system.

The amount of isocyanate compound applied to the fibrous material or related article can vary widely. Since isocyanate compounds having from as low as about 1 wt.% to over 50 wt.% isocyanate (NCO) content are available, the amount of isocyanate compound applied to the fibers is expressed herein in terms of isocyanate groups. Generally about 0.05 to about 10 wt.% of isocyanate groups or $N=C=O$ groups, based on the weight of fiber, should be applied to the fiber and preferably from about 0.2 to about 2.0 wt.% and more preferably from about 0.5 to about 1.25 wt.%.

Related to the amount of isocyanate compound on the treated fiber is the amount of isocyanate compound and polyunsaturated polymer in the treating solution. The adhesion system treating solution consists of from about 1 to 75 and preferably from about 5 to about 50 and more preferably from about 10 to about 35 parts by weight of the isocyanate containing compound and about 0.5 to 50 parts and preferably 1 to 20 and more preferably 1 to 10 parts per weight of the polyunsaturated polymers, maintaining the ratios of isocyanate groups to polyunsaturated polymer reactive terminal or side groups as stated below in this summary, with the remainder of the solution being plasticizer. The amount of isocyanate compound in the treating solution is very dependent on the isocyanate

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content of the particular compound. The ranges given above were for compounds with about 30 to 33% isocyanate content. This solution can be applied to the fibrous or related article at a pickup of from about 1 to over 100% on the weight of the solution to treated article and preferably from about 3 to about 25 wt.% and more preferably from about 6 to 18 wt.% and even more preferably from about 10 to about 15 wt.% and even more preferably from about 11 to 12 wt.%. Amounts outside these ranges are also acceptable.

The amount of plasticizer on the treated fibrous material or related article can generally vary from none to as much as the material will accept. However, for EPDM and other difficult to bond elastomers, the combination of plasticizer, polyunsaturated compound, and polyisocyanate is necessary to give adhesion. These adhesion values are quite high, generally increasing with the amount of polymer in the compound. A range of about 2 to about 12% by weight of plasticizer on the treated fibrous material or related articles is generally preferred with about 6 to about 10% being most preferred. Related to the amount of plasticizer on the treated article is the amount of plasticizer in the treating solution. Lower viscosity liquid plasticizers are preferred in larger amounts for ease of handling and applying the treating solution and for solubilizing the other components. Generally plasticizers, either singularly or in combination, should constitute about 10 to 90 parts by weight per 100 parts of the treating solution. The preferred range is 60 to 80 parts by weight per 100 parts of the treating solution.

Surprisingly, it has been found that very large molar ratios of isocyanate groups to reactive groups of the polyunsaturated polymers such as hydroxyl give the best adhesion results. Although there are references in the literature of the reaction of isocyanate containing compounds with hydroxyl terminated polybutadienes, the real concept of this invention has

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been overlooked. These combinations are always in equal amounts or with only relatively small excesses of isocyanate groups to hydroxyl groups. Surprisingly, it has been found that large excesses of polyisocyanates to polyunsaturated compounds impart higher adhesions to the hard to bond to synthetic elastomers such as EPDM. This is demonstrated by the examples herein such as Examples 38H-38N from Table 10. The proportion of reacted and unreacted isocyanate is calculated for Examples 38H-38N to clearly illustrate the significance of excess polyisocyanate used. It also appears that higher amounts of polyunsaturated polymers, especially if the isocyanate content is held constant or reduced, can give less adhesion improvements in some situations.

Example	Amount Desmodur VK-5 (g)	Amount Poly bd R45HT (g)	Ratio of NCO/OH	Grams OH	Grams C=C	Amount unreacted Desmodur VK-5 (g)	% Unreacted Desmodur VK-5 (g)
38H	17.20	1.60	100	0.02	0.70	17.03	99.0%
38I	17.20	3.20	50	0.09	1.40	16.86	98.0%
38J	17.20	6.30	25	0.09	2.76	16.52	96.1%
38K	17.20	15.80	10	0.22	6.92	15.50	90.1%
38L	17.20	31.80	5.0	0.45	13.93	13.79	80.2%
38M	17.20	63.20	2.5	0.89	27.69	10.42	60.6%
38N	3.70	13.50	2.6	0.19	5.92	2.25	60.9%

It appears that the actual adhesion imparting combination is excess polyisocyanate molecules plus polyisocyanate partially reacted with reactive polyunsaturated compounds.

Improved adhesion under this invention can be obtained with 2.5 to 1 or higher moles of isocyanate ($N=C=O$) to hydrocarbon polymer reactive groups. However, the higher molar ratios of isocyanate to hydrocarbon polymer reactive groups are generally preferred, namely from 5:1 or 10:1 to about 100:1, 200:1, 750:1, 1500:1, 3000:1 or higher and

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particularly from about 25:1 to 200:1 and more particularly 50:1 to 100:1.

The same relationship applies in regard to the amount of heteroatom polymer where even higher ratios of isocyanate to polymer end or reaction groups appear to be preferred. Although a range as low as 1:1 and higher
5 can be used in this invention, the range of about 25:1 or about 50:1 to 350:1 isocyanate to polymer reactive groups is generally preferred.

When the two polymers are used together with the isocyanate, then the ratio of isocyanate to reactive group for each polymer should generally increase so that a more preferred range would be about 25:1 to
10 about 250:1 for the isocyanate to hydrocarbon polymer reactive group and about 50 to 1 to about 750 to 1 for the isocyanate to heteroatom polymer terminal or reactive group when both polymers are used.

The polyunsaturated polymer used in the adhesion system of this invention can also be expressed in terms of the amount of carbon-carbon
15 double bonds on the treated articles. In that the polyunsaturated polymer can vary greatly in terms of unsaturation, such an expression is best done in wt.% of carbon-carbon double bonds on the treated article. It has been found that a total of polyunsaturated polymers as low as 0.034 wt.%, based carbon-carbon double bonds, on the weight of the treated article, provides
20 a significant improvement in adhesion. Even lower amounts, such as 0.0075 wt.%, can be expected to provide adhesion improvements. The lower limit for the effective amount of carbon-carbon double bonds will depend on the specific rubber compound used, particularly in regard to variables such as the type of polymer, the amount of polymer and the amount of filler in the
25 rubber compound to be adhered to.

Other materials may also be added to the adhesion system of this invention to perform other functions. One example is the addition of a free radical initiator or generator to facilitate bonding to the rubber and other polymers. This free radical initiator or generator will even preferably react

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with the other components of the adhesion system of this invention, either isocyanate or terminal or side groups on either polyunsaturated polymer. Such compounds include, but are not limited to, amine, hydroxyl and carboxyl terminated azo and peroxide compounds such as 2,2'-azobis(2-methyl-N-(2-hydroxyethyl)propionamide, 2,2'-azobis(2-amidinopropane)dihydrochloride, 4,4'-azobis(4-cyanopentanoic acid), dehydroxy azobenzene and similar compounds. Non-reactive free radical initiators or generators such as azo, peroxide and sulfide and sulfur compounds known in the art of initiating free radical polymerization and in the rubber vulcanization process. Other crosslinking agents such as polyepoxides, melamine-formaldehyde adducts and their ethers, urea and urea derivative-formaldehyde adducts and their ethers, phenol-formaldehyde adducts and their ethers, resorcinol-formaldehyde adducts and their ethers, and other crosslinkers known in the art can be added. Furthermore, coupling agents such as but not limited to vinyl, mercapto, methacryl, amino, ureido and epoxy silanes may be added. These chemicals can react with the components of the adhesion system of this invention through some groups and either chemically or physically, or both, with the treated fibers and related articles, especially fibers with very inactive surfaces such as glass, metals and ceramics, and with the rubber and other polymers, and especially with fillers such as silica and other minerals. Such fillers and even carbon can be also added to the components of the adhesion system of this invention. Extenders, such as naphthenic and hydrocarbon oils, when they do not function as a solvent or a plasticizer can also be added as well as other functional materials well known to those skilled in the art.

The treated yarns can be incorporated into hoses or other mechanical rubber goods by braiding, spiral wrapping or knitting processes and other conventional techniques. The treated yarns can also be converted to fabrics and other fibrous articles, which can be incorporated into mechanical rubber

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goods and related articles or be bonded directly to rubber sheets, by knitting, weaving or non-woven techniques. It is in these converting processes that the invention can be better utilized by selecting plasticizers, isocyanates and unsaturated oligomers or polymers to optimize processing in these conversion steps. Woven, non-woven or knitted fabrics, films or sheets, consisting of polymers the same as or similar to those used in filaments, yarns or fibers, can be treated by padding, coating or other well known techniques to be incorporated into rubber composites or bonded to rubber sheets.

The treated fibrous materials of the invention can be incorporated into a variety of rubber products by a variety of conventional methods, as well as by unconventional methods. Although the simplest method of reinforcing may be a rubber to fibrous or related material bond, either with the fibrous material wrapped around the rubber material as in a hose or a tube or with the fibrous material next to the rubber material in a sheet-like assembly such as in conveyor belts or the like, any type of structure such as but not limited to rubber-fibrous material-rubber, rubber-fibrous material-rubber-fibrous material, rubber-fibrous material-rubber-fibrous material-rubber and so on is contemplated for the adhesion system of this invention. Such assemblies can be used for the many types of hoses, tubes and related articles, including but not limited to automotive hoses such as brake hoses, power steering hoses, coolant hoses and the like, washing machine hoses, garden hoses, fire hoses, gasoline hoses, welding hoses, oil suction hoses, optical cables, electrical cables and the like. Such assemblies can also be used for the many other types of rubber products including but not limited to conveyor belts, automotive and other drive belts such as V belts, "stiff" cord belts and the like, automotive and other vehicle tires including but not limited to tractors, "off-the-road" vehicles, airplanes, motorcycles, bicycles, wheelchairs and the like, rubber reinforced fabrics, pads, molded articles, geotextiles such as pond and land fill liners, silt and erosion control, filtration media for French drains and the like, tank liners, tank insulation matting, roofing mem-

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branes, cow and other animal mats, vibrational damping pads, air inflated shock absorbing units, reinforced rubber bags for various gas and liquid collection and other composite articles such as rods, masts, bars and the like.

5 The adhesion system of this invention can also be used as described above to impart adhesion to products containing polymers other than the rubber polymers, as long as these polymers are capable of bonding with the components of the adhesion system of this invention in the same manner as the rubber polymers. More particularly, non-rubber polymers
10 which contain carbon-carbon double bonds or groups which are capable of producing such double bonds or groups which can react with the free radical producing agents or other vulcanizing or crosslinking agents should have increased adhesion with articles treated with the adhesive system of this invention. Such polymers can include but are not limited to unsaturated
15 polyesters, unsaturated polyamides, unsaturated polythioesters, polynorbornenes, unsaturated polyethers, randomly unsaturated polyolefins, non-rubber copolymers such as acrylic and methacrylic acid, ester and amides, alkyl vinyl ethers and other vinyl monomers such as styrene, vinyl pyridine, vinyl pyrrolidone and the like containing diene units and the
20 like.

 In addition to bonding to the various polymers described above, the adhesion system of this invention can even bond to itself, either alone or in combination with a rubber or non-rubber polymer. This bonding can be facilitated by the addition of bonding agents, either from an external
25 application or by an internal application as described elsewhere in this summary. Such bonding can be in composite articles with very little matrix material, such as but not limited to sail masts, golf clubs, fishing rods, automotive and airplane assemblies, rocket nozzles and the like where high strength fibers and fabrics and other articles made from these

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fibers such as carbon, glass, ceramic, and organic aramid, high strength polyolefin and others as described below are aligned very closely in a matrix.

5 It is envisioned that any organic or inorganic fiber or related material can be treated with compounds of this invention. Organic fibers include, but are not limited to, polyester (polyethylene terephthalate, polybutylene terephthalate, polycyclohexanedimethanoterephthalate, and related polymers), nylon 6, nylon 66 and other nylons, cotton, rayon, Tencel™, Lyocel cellulosic fibers, Mewlon®, Kuralon® and other polyvinyl alcohol
10 fibers, Nomex®, Kelvar®, Twaron® and Technora® aramid fibers, polybenzimidazole (PBI) fibers, polypropylene, polyethylene and other polyolefin, ultra high strength polyolefins, polyphenylene sulfide wool, silk, ramie, flax and blends and mixtures thereof. Inorganic fibers include, but are not limited to carbon, glass, metal and ceramic fibers and blends and
15 mixtures thereof and with organic fibers. Exact formulations of the various components of the invention, such as amount of isocyanate compound and plasticizer type can be optimized for particular fibers or classes of fibers.

20 The treated yarns and other materials of the invention should give improved adhesion when incorporated into a wide variety of rubber products consisting of all of the natural and synthetic rubber and synthetic elastomers and thermoplastic elastomers as described in *Martin Grayson/ Executive Editor, Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 8, Wiley-Interscience, New York; and Maurice Morton - Editor,
25 *Rubber Technology*, 2nd Edition, Van Nostrand Reinhold Co. (1973); N.P. Cheremisinoff, *Elastomer Technology Handbook*, CRC Press Inc. (1993). Such rubber-like polymers include, but are not limited to, natural rubber (NR), polyisoprene (IR) and copolymers of isoprene, polybutadiene (BR), styrene butadiene rubber (SBR), acrylonitrile butadiene rubber (NBR) and

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other copolymers of butadiene, polychloroprene (CR) and copolymers of chloroprene, ethylene propylene diene comonomers (EPDM), ethylene propylene rubber (EPM), chlorinated polyethylene (CPE), chlorosulfonated polyethylene (CPM), butyl rubber (BR), chlorobutyl (CBR), bromobutyl rubber (BBR), hydrogenated nitrile-butadiene rubber (HNBR), crosslinked polyethylene (XPE), silicone rubber (VMQ), fluorosilicone rubber (FVMQ), epichlorohydrin rubber (ECO), tetrafluoroethylene-propylene copolymer, and polyvinyl chloride (PVC) and blends and mixtures of the above with each other and with other polymers.

Improved adhesion to rubber can be obtained with a variety of rubber compounds, with variables in the rubber compound maybe affecting the absolute adhesion values but not affecting the result of the improved adhesion by the adhesion system of this invention. There are many types of rubber compounds, formulated with major or minor changes to achieve specified properties in the final rubber product. Examples of some rubber formulators who supply various rubber compound to mechanical rubber goods manufacturers and other rubber processors are Burke Rubber, Cadillac Rubber, Colonial Rubber and Kleen-Tex. Examples of some hose, belt, tire and other mechanical rubber goods manufacturers are Cooper Industrial Products, Dana Corporation, Dayco Products Inc., Gates Rubber Company, The Goodyear Tire and Rubber Company, HBD Industries, Parker-Hannifin Corporation and Plumley Industries. Some of these manufacturers also formulate their own rubber compounds.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, all temperatures are

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set forth uncorrected in degrees Celsius and unless otherwise indicated, all parts and percentages are by weight.

The entire disclosures of all applications, patents and publications, cited above and below, are hereby incorporated by reference.

EXAMPLES

EXAMPLE 1

As a control and as a general procedure for the following examples, A.C.S. certified toluene was applied by a slot applicator to 1000 denier, 1.5 TPI polyester continuous filament yarn (AKZO Diolen Type 174S) and wound onto 6 3/4" long, 1 1/2" inside diameter paper tubes on a direct drive winder at a speed of about 90 yards per minute. A Masterflex peristaltic pump using #14 Viton tubing was used to deliver the treating solution to the yarn at a rate of 1.23 grams toluene per minute to give a pickup of the solution on the yarn of 12 wt.%. After about 1000 to 1100 yards of yarn were wound, the tube was removed from the winder. After about four to twelve hours under ambient conditions, the tube was placed in a walk-in oven at 200°F for 220 minutes followed by a 20 minute cool down cycle to about 120°F. The tubes were then removed from the oven about four hours later and allowed to cool and condition at ambient conditions before testing.

EXAMPLE 2

Example 1 was repeated except that the treating solution was 20.75 parts by weight of toluene added to 79.25 parts by weight of dioctyl terephthalate (Kodaflex® DOTP, Kodaflex® is a trademark of Eastman Chemical Company).

The treating solution was made by adding the toluene to the dioctyl terephthalate and mixing until homogenous. The mixing was done by using a stirring bar and a magnetic stirrer. A stirring rod was used if the magnetic stirrer was not sufficient in producing a homogeneous solution.

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EXAMPLE 3

Example 2 was repeated except that the treating solution was 20.74 parts of toluene added to 79.25 parts dibutyl phthalate (Kodaflex DBP from Eastman Chemical Company).

5 EXAMPLE 4

Example 2 was repeated except that the treating solution was 20.75 parts of toluene added to 79.24 parts dioctyl adipate (di-2-ethylhexyl adipate) (Kodaflex DOA from Eastman Chemical Company).

EXAMPLE 5

10 Example 2 was repeated except that the treating solution was 13.0 parts of tolylene-2,4-diisocyanate (Eastman Chemical Company #06590P, CAS #584-84-9) added to 87.0 parts toluene.

EXAMPLE 6

15 Example 5 was repeated except that the treating solution was 12.59 parts of hexamethylene diisocyanate (Eastman Chemical Company #06735, CAS #822-06-0) was added to 87.41 parts of toluene.

EXAMPLE 7

20 Example 5 was repeated except that the treating solution was 19.19 parts of polymethylene polyphenyl isocyanate with approximately 32.5% isocyanate content and an approximate viscosity of 40 centipoise (Desmodur VKS-4 from Miles Inc.) added to 80.90 parts of toluene. Then 0.39 parts toluene was added to the mixture to obtain a 19.1% solution.

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EXAMPLE 8

Example 7 was repeated except that 19.1 parts of Desmodur VK-5 from Miles Inc. (polymethylene polyphenyl isocyanate with approximately 32.5% isocyanate content and an approximate viscosity of 50 centipoise) was added to 80.9 parts of toluene.

EXAMPLE 9

Example 7 was repeated except that 20.0 parts of Desmodur VK-18 from Miles Inc. (polymethylene polyphenyl isocyanate with approximately 31.5% isocyanate content and an approximate viscosity of 180 centipoise) was added to 80.0 parts of toluene.

EXAMPLE 10

Example 7 was repeated except that 20.0 parts of Desmodur VKS-18 from Miles Inc. (polymethylene polyphenyl isocyanate with approximately 31% isocyanate content and an approximate viscosity of 180 centipoise) was used in place of Desmodur VK-18.

EXAMPLE 11

Example 7 was repeated except that 21.9 parts of Desmodur VK-70 from Miles Inc. (polymethylene polyphenyl isocyanate with approximately 31% isocyanate content and an approximate viscosity of 700 centipoise) was added to 78.1 parts of toluene.

EXAMPLE 12

Example 7 was repeated except that 23.97 parts of Desmodur VK-200 from Miles Inc. (polymethylene polyphenyl isocyanate with approximately 30.6% isocyanate content and an approximate viscosity of 2000 centipoise) was added to 76.00 parts of toluene.

EXAMPLE 13

All treated continuous yarn fiber samples in these examples were evaluated for adhesion properties by winding each treated sample from its wound tube onto 4" wide masking tape (Anchor) wrapped around, with
5 adhesive side up, a rotatable stainless steel drum that had replaced the standard flat plate on a Serriplane manufactured by Alfred Suter, Inc., so that three 1 1/3" wide fiber samples, either the same or different yarn samples, were put on one tape. Each yarn sample was wound so that there was no overlapping of filaments and no space between adjacent fila-
10 ments. This drum was 6" long, of 6" diameter and had one thin slot across the length. The tape containing the three wound yarn samples was then removed from the drum by cutting across the slot on the drum with a razor blade. The 4" wide tape containing three samples was then cut into four 4" lengths.

15 Two clean 4" X 8 1/2" pieces of an unvulcanized compounded rubber, which had been milled to a specified thickness, were placed side by side touching to form a 8" x 8 1/2" square centered on a 10" X 10" aluminum plate. This plate had been preheated to the vulcanization temperature for the specific rubber compound. A 1" X 9" strip of aluminum foil was
20 placed on the outside edge of each 4" x 8 1/2" piece of compounded rubber. Two fiber tape sections containing three fiber samples each were then placed fiber side down on each 4" X 8 1/2" rubber pad so that the fibers were perpendicular to the aluminum foil and about one inch of their length covered the aluminum foil strip. The top 10" X 10" aluminum plate
25 which had also been preheated to the vulcanization temperature for the specific rubber compound was placed on top of the samples so that a sandwich of top plate, tape, yarn samples, rubber compound and bottom plate was formed. This sandwich was then placed in a PHI model # 02 38 C-X7 hydraulic press at the vulcanization temperature for the specific

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5 rubber compound for the specified time for that particular compound at 3200 lbf. The pad was removed after cure and allowed to cool and condition at ambient conditions for 16 to 24 hours. After conditioning, each pad was cut into six 1" X 4" strips by measuring 3/16" from the edge of the tape of the first strip, cutting the first one inch strip, measuring 3/16" to the second sample, cutting the second one inch strip, and so on. The aluminum foil strip, which functioned to give a starting separation between the yarn samples and the rubber compound, was removed from each strip and discarded. If the foil could not be removed, it was left in the strip.

10 Each 1" x 4" composite strip was tested on a Lloyd 500 tensile machine. The distance from the lower jaw to the upper jaw was set at one inch. Each sample strip was then placed horizontally in the tensile tester with the fiber side being attached to the upper jaw and the rubber side being attached to the lower jaw. The tester was set to a traversing speed of two inches per minute and started. The mean and maximum load required to separate the fiber from the rubber was determined by a computer attached to the tester. After each adhesion pull was complete, each pad was inspected for the mode of separation and the length of separation.

15 Fiber-to-rubber separation means that the separated area showed mainly fiber with no or only a few small pieces of rubber adhered. Rubber-to-rubber separation means that the separated area showed mainly rubber with no or only a few fibers visible. Mixed fiber-to-rubber and rubber-to-rubber separation means that there were significant amounts of both fiber and rubber adhered to fiber in the separated area. A shorter separation length was observed to show increased difficulty in separating the yarn and rubber sections, indicating higher adhesion. Shorter separation lengths were usually accompanied by stretching of the rubber. In cases where duplicate tests with the same yarn and same rubber compound

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were made, each of the above parameters were averaged and reported in the table.

EXAMPLE 14

5 The treated yarn samples from Examples 1 through 12 were tested
for adhesion properties according to the procedure of Example 13. A
carbon filled EPDM compound used in commercial hoses milled to a thick-
ness of about 0.060 inches was the rubber compound used. The vulcani-
zation conditions were 325°F for 30 minutes at 3200 PSI pressure. The
data in Table 1 was obtained which shows that yarn treated with only the
10 separate components of the adhesion system of this invention exhibit low
adhesion to the rubber.

TABLE 1

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
1	Non-additive solvent control	0.54	1.08	Fiber to Rubber	43
2	Toluene-containing Dioctyl Terephthalate Plasticizer Only	0.38	0.72	Fiber to Rubber	45
3	Toluene-containing Dibutyl Phthalate Plasticizer Only	0.00	0.00	Fiber to Rubber	73
4	Toluene-containing Dioctyl Adipate Plasticizer Only	0.88	1.38	Fiber to Rubber	47
5	Toluene-containing Toluene Diisocyanate Only	0.78	1.53	Fiber to Rubber	40
6	Toluene-containing Hexamethylene Diisocyanate Only	1.13	2.40	Fiber to Rubber	37
7	Toluene-containing Desmodur VK-4 Only	3.72	4.38	Fiber to Rubber	42
8	Toluene-containing Desmodur VK-5 Only	2.87	3.48	Fiber to Rubber	42
9	Toluene-containing Desmodur VK-18 Only	4.17	4.91	Fiber to Rubber	41
10	Toluene-containing Desmodur VK-18 Only	4.37	4.98	Fiber to Rubber	41
11	Toluene-containing Desmodur VK-70 Only	5.33	6.58	Mixed (Thin)	40
12	Toluene-containing Desmodur VK-200 Only	4.52	5.18	Mixed	40

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EXAMPLE 15

Example 14 was repeated except that a different carbon filled EPDM compound used in commercial hoses milled to a thickness of about 0.100 to 0.120 inches was used. The vulcanization conditions were 320°F for 25 minutes at 3200 PSI pressure. The results are shown in Table 2.

5

TABLE 2

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
1	Non-additive solvent control	0.79	1.58	Fiber to Rubber	50
2	Toluene-containing Dioctyl Terephthalate Plasticizer Only	0.73	1.46	Fiber to Rubber	49
3	Toluene-containing Dibutyl Phthalate Plasticizer Only	0.80	1.60	Fiber to Rubber	42
4	Toluene-containing Dioctyl Adipate Plasticizer Only	0.75	1.49	Fiber to Rubber	39
5	Toluene-containing Toluene Diisocyanate Only	0.32	0.63	Fiber to Rubber	55
6	Toluene-containing Hexamethylene Diisocyanate Only	0.79	1.58	Fiber to Rubber	45
8	Toluene-containing Desmodur VK-5 Only	1.58	3.31	Fiber to Rubber	44
9	Toluene-containing Desmodur VK-18 Only	2.35	4.00	Fiber to Rubber	44
11	Toluene-containing Desmodur VK-70 Only	2.46	4.13	Fiber to Rubber	44
12	Toluene-containing Desmodur VK-200 Only	2.20	3.47	Fiber to Rubber	44

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The data in Table 2 shows that yarn treated with only the separate components of the adhesion system of this invention also exhibit the same low adhesion to a different EPDM rubber as in Table 1.

EXAMPLE 16

5 Example 7 was repeated with the exception that the treating solution was 20.0 parts of Desmodur VKS-18 added to a solution of 75.0 parts dioctyl terephthalate (Kodaflex DOTP from Eastman Chemical Company) and 5.0 parts toluene.

EXAMPLE 17

10 Example 2 was repeated except that the treating solution was 95.0 parts of toluene added to 5.0 parts hydroxyl terminated-1,3-butadiene homopolymer (CAS# 69102-90-5) having a number average molecular weight of approximately 2,800, a hydroxyl number of 0.83 meq/g, and an unsaturation of 20% cis-1,4, 60% trans-1,4, and 20% vinyl-1,2,
15 (Poly bd R45HT from Atochem North America).

EXAMPLE 18

 Example 2 was repeated except that the treating solution was 75.0 parts dioctyl terephthalate (Kodaflex DOTP from Eastman Chemical Company) added to 5.0 parts hydroxyl terminated-1,3-butadiene homopolymer
20 from Example 17 and 20.0 parts of toluene.

EXAMPLE 19

 Example 17 was repeated except that the treating solution was 20.0 parts Desmodur VKS-18 added to a solution of 5.0 parts of the hydroxyl terminated-1,3-butadiene homopolymer dissolved in 75.0 parts
25 toluene.

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EXAMPLE 20

Example 19 was repeated except 75.0 parts dioctyl terephthalate replaced the toluene.

EXAMPLE 21

5 The treated yarn samples from Examples 16 through 20 were tested for adhesion properties according to the procedure of Example 13. The same EPDM compound from Example 14 but milled to a thickness of approximately 0.100 to 0.120 inches was used. The vulcanization conditions were 325°F for 30 minutes at 3200 PSI pressure. The results are
10 shown in Table 3.

TABLE 3

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
16	Isocyanate and Plasticizer and Toluene	3.06	4.36	Fiber to Rubber	42
17	Toluene-containing Hydroxyl Terminated Polybutadiene Only	0.90	1.92	Fiber to Rubber	33
18	Hydroxyl Terminated Polybutadiene and Plasticizer and Toluene	0.80	1.54	Fiber to Rubber	36
19	Isocyanate and Hydroxyl Terminated Polybutadiene and Toluene	12.11	13.98	Rubber to Rubber	32
20	Isocyanate and Hydroxyl Terminated Polybutadiene and Plasticizer	13.17	14.66	Rubber to Rubber	30

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5 The data in Table 3 shows that yarn treated with the combination of components consistent with the adhesion system of this invention (Examples 19 and 20) exhibits significantly improved adhesion in terms of higher mean and maximum loads, failure type and shorter pull length, to the EPDM rubber compared to other compositions.

EXAMPLE 22

10 The treated yarn samples from Examples 16 through 20 were tested for adhesion properties according to the procedure of Example 13. The same EPDM compound from Example 15 was used. The vulcanization conditions were 320°F for 25 minutes at 3200 PSI pressure. The results are shown in Table 4.

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TABLE 4

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
16	Isocyanate and Plasticizer and Toluene	2.69	3.67	Fiber to Rubber	45
17	Toluene-containing Hydroxyl Terminated Polybutadiene Only	0.91	1.78	Fiber to Rubber	45
18	Hydroxyl Terminated Polybutadiene and Plasticizer and Toluene	1.26	2.40	Fiber to Rubber	45
19	Isocyanate and Hydroxyl Terminated Polybutadiene and Toluene	25.85	33.37	Rubber to Rubber	31
20	Isocyanate and Hydroxyl Terminated Polybutadiene and Plasticizer	32.54	36.55	Rubber to Rubber	25

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The data in Table 4 shows that yarn treated with a combination of components consistent with the adhesion system of the present invention (isocyanate, carrier (plasticizer/solvent) and polyunsaturated polymer) exhibits even more improvement in adhesion to a different EPDM rubber than in Table 3.

EXAMPLE 23

The treated yarn samples from Examples 16 through 20 were tested for adhesion properties according to the procedure of Example 13. A commercial EPDM compound used in commercial hoses, similar to that used in Example 21 but containing less EPDM and more filler was used. It also was milled to a thickness of approximately 0.100 to 0.120 inches. The vulcanization conditions were 325°F for 30 minutes at 3200 PSI pressure. The results are shown in Table 5.

TABLE 5

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
16	Isocyanate and Plasticizer and Toluene	9.05	10.43	Rubber to Rubber	33
17	Toluene-containing Hydroxyl Terminated Polybutadiene Only	1.41	2.71	Fiber to Rubber,	43
18	Hydroxyl Terminated Polybutadiene and Plasticizer and Toluene	1.37	2.09	Fiber to Rubber	42
19	Isocyanate and Hydroxyl Terminated Polybutadiene and Toluene	10.22	12.56	Rubber to Rubber	32
20	Isocyanate and Hydroxyl Terminated Polybutadiene and Plasticizer	12.57	13.94	Rubber to Rubber	32

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5 The data in Table 5 also shows that yarn treated with the combination of components consistent with the adhesion system of the present invention (isocyanate, carrier (plasticizer/solvent) and polyunsaturated polymer) exhibits the highest adhesion to the EPDM rubber compared to other combinations.

EXAMPLE 24

10 Example 2 was repeated with the exception that the treating solution used was 20.0 parts of toluene added to 80.0 parts of the mixture of 80% bis(2-ethylhexyl) terephthalate (dioctylterephthalate (DOTP) CAS# 6422-86-2) and 20% poly(2,2,4-trimethyl-1,3-pentanediol maleate) (CAS# 250-5-65-8) (Kodaflex PA-6 from Eastman Chemical Company).

EXAMPLE 25

15 Example 24 was repeated with the exception that the treating solution used was 20.0 parts of toluene added to a mixture of 75.0 parts of the mixture of 80% bis(2-ethylhexyl) terephthalate and 20% poly(2,2,4-trimethyl-1,3-pentanediol maleate) and 5.0 parts of the hydroxyl terminated polybutadiene used in Example 17.

EXAMPLE 26

20 Example 24 was repeated except that the treating solution was 20.0 parts of Desmodur VKS-18 added to a solution of 75.0 parts of the mixture of 80% bis(2-ethylhexyl) terephthalate and 20% poly(2,2,4-trimethyl-1,3-pentanediol maleate) mixed with 5.0 parts toluene.

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EXAMPLE 27

Example 25 was repeated except that the treating solution was 20.0 parts of Desmodur VKS-18 added to a solution of 37.5 parts of dioctylterephthalate (DOTP) (CAS# 6422-86-2) and 37.5 parts of the mixture of 80% bis(2-ethylhexyl) terephthalate and 20% poly(2,2,4-trimethyl-1,3-pentanediol maleate) mixed with 5.0 parts of the hydroxyl terminated polybutadiene (Poly bd R45HT).

EXAMPLE 28

The treated yarn samples from Examples 24, 25, 26 and 27 were tested for adhesion properties according to the procedure of Example 13. The same carbon filled EPDM compound from Example 15 was used. The vulcanization conditions were 320°F for 25 minutes at 3200 PSI pressure. The results are shown in Table 6.

TABLE 6

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
24	Toluene-containing Poly Maleate Ester and Plasticizer Only	1.15	2.23	Mixed	52
25	Toluene-containing Poly Maleate Ester and Plasticizer and Hydroxyl Terminated Polybutadiene	0.93	1.92	Fiber to Rubber	41
26	Isocyanate and Poly Maleate Ester and Plasticizer and Toluene	7.65	8.75	Fiber to Rubber	41
27	Isocyanate and Poly Maleate Ester and Plasticizer and Hydroxyl Terminated Polybutadiene	34.79	39.25	Rubber to Rubber	26

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5 The data in Table 6 shows that yarn treated with the combination of components consistent with the present invention (isocyanate, carrier (plasticizer/solvent) and polyunsaturated polymers) exhibit higher adhesion to the EPDM compound compared to the other combinations of components and that mixtures of hydroxy-terminated polybutadiene and polymaleate ester provided treated yarns with the highest adhesion to the EPDM compound.

EXAMPLE 29

10 The treated yarn samples from Examples 16, 17, 18, 19, 20, 24, 25, 26 and 27 were tested for adhesion properties according to the procedure of Example 13. A carbon filled neoprene compound used in commercial hoses milled to a thickness of about 0.100 to 0.120 inches was the rubber compound used. The vulcanization conditions were 325°F for 30 minutes at 3200 PSI pressure. The results are shown in Table 7.

TABLE 7

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
16	Isocyanate and Plasticizer and Toluene	12.17	13.38	Rubber to Rubber	40
17	Toluene-containing Hydroxyl Terminated Polybutadiene Only	0.62	1.24	Fiber to Rubber	71
18	Hydroxyl Terminated Polybutadiene and Plasticizer and Toluene	1.57	2.33	Fiber to Rubber	50
19	Isocyanate and Hydroxyl Terminated Polybutadiene and Toluene	8.60	9.67	Mixed	40
20	Isocyanate and Hydroxyl Terminated Polybutadiene and Plasticizer	12.21	13.36	Rubber to Rubber	40
24	Toluene-containing Poly Maleate Ester and Plasticizer Only	1.30	2.06	Fiber to Rubber	47
26	Isocyanate and Poly Maleate Ester and Plasticizer and Toluene	12.40	13.34	Rubber to Rubber	37
27	Isocyanate and Poly Maleate Ester and Hydroxyl Terminated Polybutadiene and Plasticizer	13.51	15.13	Mixed	37

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5 The data in Table 7 shows that yarn treated with the conventional adhesion system of isocyanate and plasticizer (Example 16) gives higher adhesion to neoprene, one of the older synthetic rubbers, than to EPDM, one of the more difficult to adhere to synthetic elastomers (Table 6) but the adhesion system of this invention (Examples 19, 20, 26 and 27) gives the same or higher adhesion than the conventional adhesion system on neoprene.

EXAMPLE 30

10 Example 19 was repeated except that the treating solution used was 13.06 parts of tolylene-2,4-diisocyanate (from Example 5) added to a mixture of 5.02 parts Poly bd R45HT (from Example 17) added to 81.99 parts toluene.

EXAMPLE 31

15 Example 30 was repeated except that the treating solution used was 12.59 parts of hexamethylene diisocyanate (from Example 6) added to a mixture of 5.01 parts Poly bd R45HT added to 82.39 parts toluene.

EXAMPLE 32

20 Example 30 was followed except that the treating solution used was 19.10 parts of Desmodur VK 5 (from Example 8) added to a mixture of 5.01 parts Poly bd R45HT added to 75.89 parts toluene.

EXAMPLE 33

Example 32 was followed except that the treating solution used was 20.01 parts of Desmodur VKS-18 (from Example 10) added to a mixture of 4.99 parts Poly bd R45HT added to 74.99 parts toluene.

EXAMPLE 34

Example 32 was followed except that the treating solution used was 21.91 parts of Desmodur VK-70 (from Example 11) added to a mixture of 4.99 parts Poly bd R45HT added to 73.09 parts toluene.

5

EXAMPLE 35

Example 32 was followed except that the treating solution used was 24.01 parts of Desmodur VK -200 (from Example 12) added to a mixture of 4.99 parts Poly bd R45HT added to 71.00 parts toluene.

EXAMPLE 36

10

The treated yarn samples from Examples 30 through 35 were tested for adhesion properties according to the procedure of Example 13. The same carbon filled EPDM compound milled to the same thickness as in Example 14 was used. The vulcanization conditions were 325°F for 30 minutes at 3200 PSI pressure. The results are shown in Table 8.

TABLE 8

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
30	Toluene-containing Toluene Diisocyanate & Hydroxyl Terminated Polybutadiene	3.54	4.24	Mixed	42
31	Toluene-containing Hexamethylene Diisocyanate & Hydroxyl Terminated Polybutadiene	4.73	7.73	Mixed	41
32	Toluene-containing Desmodur VK-5 & Hydroxyl Terminated Polybutadiene	8.62	10.07	Mixed With Less Fiber to Rubber and More Rubber to Rubber	34
33	Toluene-containing Desmodur VKS-18 & Hydroxyl Terminated Polybutadiene	9.09	11.07	Rubber to Rubber	34
34	Toluene-containing Desmodur VK-70 & Hydroxyl Terminated Polybutadiene	10.33	11.55	Rubber to Rubber	31
35	Toluene-containing Desmodur VK-200 & Hydroxyl Terminated Polybutadiene	10.29	11.33	Rubber to Rubber	31

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The data in Table 8 shows that significant adhesion to EPDM is exhibited by yarn treated with adhesion systems of this invention where a solvent is used as the carrier component.

EXAMPLE 37

5 The treated yarn samples from Examples 30, 31, 32, 34 and 35 were tested for adhesion properties according to the procedure of Example 13. A carbon filled chlorobutyl compound used in commercial hoses milled to a thickness of about 0.100 to 0.120 inches was the rubber compound used. The vulcanization conditions were 310°F for 40 minutes at 3200
10 PSI pressure. The data in Table 9 was obtained.

TABLE 9

Example	Composition	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
30	Toluene-containing Toluene Diisocyanate & Hydroxyl Terminated Polybutadiene	3.56	4.73	Fiber to Rubber	42
31	Toluene-containing Hexamethylene Diisocyanate & Hydroxyl Terminated Polybutadiene	3.99	4.79	Fiber to Rubber	42
32	Toluene-containing Desmodur VK-5 & Hydroxyl Terminated Polybutadiene	12.51	14.14	Mixed	35
34	Toluene-containing Desmodur VK-70 & Hydroxyl Terminated Polybutadiene	13.73	15.75	Rubber to Rubber	35
35	Toluene-containing Desmodur VK-200 & Hydroxyl Terminated Polybutadiene	5.65	7.76	Fiber to Rubber	42

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The data in Table 9 shows that significant increase in adhesion to the chlorobutyl rubber is exhibited by yarn treated with adhesion systems of this invention where a solvent is used as the carrier.

EXAMPLE 38

5 Table 10 shows a comparison of a solvent as a carrier versus a plasticizer as a carrier over a range of molar ratios of isocyanate to terminal groups of hydrocarbon polymer. In this Table, the amount of Poly bd R45HT specified was added to either the amount of toluene as a solvent-carrier or the amount of di-2-ethylhexyl adipate (Kodaflex DOA) as specified in Table 10. After stirring as in Example 2 to obtain a homogeneous solution, the amount of Desmodur VK-5 as specified in Table 10 was added and the resulting mixture again made homogeneous and applied to the Type 174S polyester yarn as in Example 1. The treated yarns were tested for adhesion by the procedure of Example 13 using the same carbon filled EPDM compound as in Example 15. The vulcanization conditions were 320°F for 25 minutes at 3200 psi. The adhesion results for the varying ratios are shown in Table 10.

20 In Table 10, the molar ratios of isocyanate (NCO) to hydroxyl group (OH) were calculated using Desmodur VK-5 (from Example 8) with a 32.5% isocyanate content and Poly bd R45HT (from Example 17) with a hydroxyl value of 0.83 meq OH/g and a calculated hydroxyl number (OH#) of 46.563 meq KOH/g by calculating equivalent ratios and translating to molar ratios by the following equations:

Equivalent Weight, EW = grams/equivalents

25 $EW = 4202/\%NCO$; Formula Weight NCO = 42.02 g

EW = 56,100/OH# ; Formula Weight KOH = 56.1 g

Hydroxyl Value = meq OH/g

$$\text{OH\#} = \text{meq OH/g} \times \text{meq KOH/meq OH} \times 56.1 \text{ mg KOH/meq KOH}$$

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Equivalent Ratio (NCO/OH) = Equivalents NCO/Equivalents OH =
 (grams NCO/EWNCO)/(grams OH/EWOH)

Molar Ratio (NCO/OH) = Moles NCO/Moles OH = eq NCO/eq OH
 x mole NCO/eq NCO x eq OH/mole OH

5 Sample calculation for Example 38H

OH#R45HT = (0.83 meq OH/g) x (meq KOH/meq OH) x (56.1 mg
 KOH/meq KOH)

grams Poly bd R45HT = 1.60

grams Desmodur VK-5 = 17.20

10 EWR45HT = 56,100/(0.83 x 56.1)

EWVK-5 = 4202/32.5

Equivalent Ratio (NCO/OH) =

$[(17.20 \text{ g})/(4202/32.5)\text{geq}^{-1}]/[(1.60\text{g})/(56,100/(0.83 \times 56.1))\text{geq}^{-1}]$

Equivalent Ratio (NCO/OH) = 0.1330319eq NCO/0.0013278eq OH

15 Molar Ratio (NCO/OH) = [0.1330319eq NCO/0.0013278eq OH] x
 [mole NCO/eq NCO] x [eq OH/mole OH]

Molar ratio (NCO/OH) = 100 mole NCO/mole OH

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TABLE 10

EXAMPLE	DESMODUR VK-5 (Weight Per Cent)	POLY BD R4SHIT (Weight Per Cent)	TOLUENE (Weight Per Cent)	DIOCTYL ADIPATE (Weight Per Cent)	MOLAR RATIO ISOCYA- NATE TO HYDROXYL	MEAN LOAD (lb.)	MAXIMUM LOAD (lb.)	FAILURE TYPE	PULL LENGTH (mm)
38A	17.2	0	82.8	0	NA	1.44	2.26	FIBER TO RUBBER	40
38B	17.2	3.2	79.6	0	50 TO 1	8.51	12.44	MIXED	39
38C	17.2	15.8	67.0	0	10 TO 1	8.85	10.83	MIXED	39
38D	17.2	31.6	51.2	0	5 TO 1	9.45	11.86	MIXED-THIN	39
38E	17.2	63.2	19.6	0	2.5 TO 1	6.40	7.22	MIXED	42
38F	3.7	13.5	82.8	0	2.5 TO 1	8.80	12.21	MIXED	40
38G	17.2	0	0	82.8	N/A	6.62	7.49	FIBER TO RUBBER	43
38H	17.2	1.6	0	81.2	100 TO 1	16.09	25.03	MIXED-THIN	37
38I	17.2	3.2	0	79.6	50 TO 1	29.52	35.39	RUBBER TO RUBBER	29
38J	17.2	6.3	0	76.5	25 TO 1	27.31	33.90	RUBBER TO RUBBER	31
38K	17.2	15.8	0	67.0	10 TO 1	30.50	35.97	RUBBER TO RUBBER	28
38L	17.2	31.6	0	51.2	5 TO 1	16.56	20.75	MIXED-THIN	30
38M	17.2	63.2	0	19.6	2.5 TO 1	8.56	11.43	MIXED-THIN	39
38N	3.7	13.5	0	82.8	2.5 TO 1	9.51	12.21	MIXED	40

EXAMPLE 39

The concept of the effect of the molar ratio of isocyanate groups to reactive groups on the polybutadiene diol from Example 38 is demonstrated further in Table 11 using a different isocyanate (Desmodur VK-18) and using a plasticizer (dioctyl terephthalate or Kodaflex DOTP). The method of solution preparation, yarn treatment, yarn heat treatment and testing was the same as in Example 38. Examples 39A through 39F used the same EPDM compound and vulcanization conditions as in Example 38. Examples 39G through 39L used a specially prepared EPDM compound which had been milled to about 0.100 to about 0.120 inches thickness. The vulcanization conditions for Examples 39G through 39L were 330°F for 30 minutes at 3200 lbs. pressure.

Table 11 not only demonstrates again the unexpected advantage of higher adhesion with an excess of isocyanate compound present in the treating solution of the novel adhesion system, but also shows that a higher weight percent concentration of isocyanate groups on the treated article gives higher adhesion at the same ratio of isocyanate groups to butadiene polymer reactive terminal groups (Examples 39H through 39L versus Examples 39B through 39F).

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TABLE 11

EXAMPLE NO.	DESMODUR VK-18 (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	DIOCTYL TEREPHTHALATE (% BY WEIGHT)	MOLAR RATIO ISOCYANATE TO HYDROXYL GROUPS	MEAN LOAD (lb.)	MAXIMUM LOAD (lb.)	FAILURE TYPE	PULL LENGTH (mm)
39A	25.0	0	75.0	INFINITY	4.44	6.13	Fiber to Rubber	43
39B	2.53	22.47	75.0	1 to 1	10.42	18.86	Mixed	41
39C	6.31	18.69	75.0	3 to 1	27.76	35.10	Rubber to Rubber	32
39D	9.00	16.00	75.0	5 to 1	25.38	32.81	Rubber to Rubber	33
39E	13.24	11.76	75.0	10 to 1	26.57	35.53	Rubber to Rubber	33
39F	22.96	2.04	75.0	100 to 1	30.41	37.09	Rubber to Rubber	29
39G	12.5	0	87.5	INFINITY	0.89	1.61	Fiber to Rubber	39
39H	1.26	11.24	87.5	1 to 1	5.72	9.86	Mixed But More Fiber to Rubber than Rubber to Rubber	41
39I	3.15	9.35	87.5	3 to 1	9.20	17.42	Mixed	36
39J	4.50	8.00	87.5	5 to 1	14.77	23.92	Mixed	33
39K	6.62	5.88	87.5	10 to 1	17.12	24.88	Rubber to Rubber	29
39L	11.48	1.02	87.5	100 to 1	9.28	10.91	Mixed	36

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EXAMPLE 40

Following Example 1 in United States Patent Number 3,941,909 issued to Schoen et al., 150 ml of toluene was added to a beaker containing 39.16 grams of hydroxyl terminated polybutadiene (Poly bd R45HT Resin as in Example 17). The hydroxyl terminated polybutadiene was completely dissolved in the toluene using a magnetic stirrer and stirring rod as in Example 2. While this solution was stirring, 6.10 grams of tolylene-2,4-diisocyanate [TDI] (as in Example 5) were added and the mixture stirred for approximately two minutes after complete addition of the TDI. This solution was then transferred to a round bottom flask, 8-10 Boileezers boiling chips [available from Fisher Scientific] were added, an Allihn condenser was connected, and the flask was placed in a heating mantle. At a medium power setting, the mixture was heated to refluxing temperature over a period of 20 minutes, the solution was maintained at a slight reflux (15-25 drops per minute) for 1 hour. After refluxing for 1 hour, the flask was removed from heat, stoppered, cooled slightly with a damp cloth for approximately 5 minutes, and immersed in cool water. At ambient temperature, the mixture was transferred to a closed container.

EXAMPLE 41

Example 40 was repeated except 5.89 grams of hexamethylene diisocyanate (as in Example 6) replaced the tolylene-2,4-diisocyanate.

EXAMPLE 42

Example 40 was repeated except 10.89 parts of polymethylene polyphenyl isocyanate (Desmodur VK-5 as in Example 8) replaced the tolylene-2,4-diisocyanate. The mixture gelled before the solution could be applied to fiber and was remade for fiber treatment in Example 45.

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EXAMPLE 43

Example 40 was repeated except 13.08 parts of Desmodur VK-18 (from Example 9) replaced the tolylene-2,4-diisocyanate. The mixture showed signs of gelling after 17 minutes at slight reflux and gelled while transferring from the distilling flask.

EXAMPLE 44

Example 40 was repeated except 14.25 parts of Desmodur VK-70 (from Example 11) replaced the tolylene-2,4-diisocyanate. The solution gelled after 45 minutes at slight reflux.

EXAMPLE 45

Examples 40, 41 and 42 were applied to 2000 denier, 1.5 TPI polyester continuous filament yarn (AKZO Diolen Type 174S) by slot applicator as in Example 19 at a rate to give 2.8% solids add-on of the prepolymer. The solution from Example 42 had gelled within six days after transferring from the reaction flask so a fresh solution was made, using the quantities in Table 12 at approximately double the amount used in Example 42, and applied approximately 15 hours after transferring from the reaction flask. Observation of the remade solution from Example 42 indicated that it began to gel approximately 72 hours after being transferred from the reaction flask. The treated packages were heat-treated and conditioned as in Example 1. The yarns were tested for adhesion as in Example 13 using the same carbon filled EPDM (Ethylene-Propylene-Diene Monomer) compound milled to the same thickness as in Example 23. The vulcanization conditions were 325°F for 30 minutes at 3200 PSI pressure. The results shown in Table 12 were obtained.

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TABLE 12

EXAMPLE	ISOCYANATE	PARTS ISOCYANATE	PARTS POLY BD R45HT	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
40	Tolyene-2,4-Diisocyanate	6.10	39.18	3.79	4.78	Fiber to Rubber	41
41	Hexamethylene Diisocyanate	5.89	39.18	3.22	3.71	Fiber to Rubber	42
42	Desmodur VK-5	21.82	78.30	3.18	3.72	Fiber to Rubber	42

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The data in Table 12 shows that yarn treated only with a pre-polymer of an unsaturated polymer and polyisocyanate in toluene consistent with U.S. Patent 3,941,909 exhibits poor adhesion to the EPDM elastomer.

5 **EXAMPLE 46**

Solutions from Examples 40 and 42 were used in preparation of Examples 46A through 46H. Each solution was applied to 2000 denier, 1.5 tpi, polyester continuous filament yarn (AKZO Diolen Type 174S) as in Example 1 at rates sufficient to give the respective pick-up levels below.

10 The samples were heat-treated and conditioned as in Example 1 and tested as in Example 13 using the same carbon filled EPDM compound as used in Example 23 milled to a thickness of about 0.100 to 0.120 inches. The vulcanization conditions were 325°F for 30 minutes at 3200 PSI pressure. The results are shown in Table 13.

TABLE 13

Example	Prepolymer Type [Parts Used]	Isocyanate Type [Parts Used]	Plasticizer Type [Parts Used]	Other [Parts Used]	Pick-up Level	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
46A	Solution as in Example 40, Tolylene-2,4-Diisocyanate [81.7]	None	Dibutyl Phthalate [43.2] C ₇ -C ₁₁ Dialkyl Phthalate ¹ [25.4] NNO ² [6.9]	None	18.1%	2.69	3.29	Fiber to Rubber	42
46B	Solution as in Example 42, Desmodur VK-5 [81.7]	None	Dibutyl Phthalate [43.2] C ₇ -C ₁₁ Dialkyl Phthalate [25.4] NNO [6.9]	None	18.1%	4.88	5.43	Mixed	41
46C	Solution as in Example 40, Tolylene-2,4-Diisocyanate [30.0]	Desmodur VK-5 [14.6]	Dibutyl Phthalate [43.7] C ₇ -C ₁₁ Dialkyl Phthalate [25.7] NNO [7.0]	None	13.9%	12.06	13.52	Rubber to Rubber	32
46D	Solution as in Example 42, Desmodur VK-5 [32.5]	Desmodur VK-5 [14.7]	Dibutyl Phthalate [43.3] C ₇ -C ₁₁ Dialkyl Phthalate [25.4] NNO [6.9]	None	14.1%	13.45	14.79	Rubber to Rubber	33
46E	Solution as in Example 40, Tolylene-2,4-Diisocyanate [30.0]	Desmodur VK-5 [14.6]	Diethyl Adipate [76.4]	None	13.9%	8.41	9.42	Mixed	37
46F	Solution as in Example 42, Desmodur VK-5 [32.5]	Desmodur VK-5 [14.7]	Diethyl Adipate [75.6]	None	14.1%	13.55	15.00	Rubber to Rubber	34
46G	Solution as in Example 40, Tolylene-2,4-Diisocyanate [30.0]	Desmodur VK-5 [14.6]	Diethyl Adipate [25.5] DOTP [20.4] TXIB ³ [25.4]	Poly Maleate Ester [5.1]	13.9%	12.69	13.86	Rubber to Rubber	34
46H	Solution as in Example 42, Desmodur VK-5 [32.5]	Desmodur VK-5 [14.7]	Diethyl Adipate [25.2] DOTP [20.16] TXIB [25.2]	Poly Maleate Ester [5.04]	14.1%	12.16	13.71	Rubber to Rubber	34

¹Palatinol® 711P from BASF Corporation²Naphthenic Neutral Oil Coastal Pale Oil from Macmillan Petroleum (Arkansas) Inc.³2,2,4-trimethyl-1,3-pentylidibutylate Kodaflex® TXIB from Eastman Chemical Company.

The data in Table 13 shows that the addition of plasticizer alone to the pre-reaction products of Examples 40 and 42 did not provide treated yarns with high adhesion to the EPDM elastomer, while the addition of plasticizer and polyisocyanate to the pre-reaction product did provide treated yarns with high adhesion to the EPDM elastomer.

This further demonstrates that excess of isocyanate beyond that needed to react with the hydroxyl terminated polybutadiene gives significantly improved adhesion.

EXAMPLE 47

Solutions from Examples 40 and 42 were remade and used as Examples 47A and 47B. For Examples 47C through 47F, a master batch solution was prepared by adding 372.12 g dibutyl phthalate [available from Eastman Chemical Company as Kodaflex® DBP (CAS# 84-74-2)], 218.72 g of a mixture of C₇ - C₁₁ dialkyl phthalate esters [available from BASF Corporation as Palatinol® 711P], and 59.14 g of a petroleum based naphthenic neutral oil [available from Macmillan Petroleum (Arkansas) Inc. as Coastal Pale Oil] to a half gallon container. The container was stoppered, and the mixture was shaken for one minute. Example solutions 47C and 47D were prepared by adding a specific amount of isocyanate (see Table 14) to a specific amount of master batch solution (see Table 14) and stirring into solution using a magnetic stirrer. After each solution was mixed thoroughly and appeared homogeneous (~ 3 minutes), the solution was ready to be applied. Example solutions 47E and 47F were prepared by dissolving Poly bd R45HT Resin from Atochem North America (as in Example 17) in a specific amount of master batch solution (see Table 14). Once a homogeneous solution was obtained, a specific amount of isocyanate was added (see Table 14) and stirred into solution using a magnetic stirrer. Samples were mixed and ready to be applied the same as Examples 47C and 47D.

TABLE 14

Example	Prepolymer Type [Parts Used]	Isocyanate Type [Parts Used]	Poly bd R45HT [Parts Used]	Plasticizer Type [Parts Used]
47A	Remade solution as in Example 40 using twice the ingredients	None	None	None
47B	Remade solution as in Example 42 using twice the ingredients	None	None	None
47C	None	Tolylene-2,4- Diisocyanate [16.5]	None	Dibutyl Phthalate ¹ [47.8] C ₇ -C ₁₁ Dialkyl Phthalate ² [28.1] NNO ³ [7.6]
47D	None	Desmodur VK-5 [16.5]	None	Dibutyl Phthalate [47.8] C ₇ -C ₁₁ Dialkyl Phthalate [28.1] NNO [7.6]
47E	None	Tolylene-2,4- Diisocyanate [16.5]	8.0	Dibutyl Phthalate [43.2] C ₇ -C ₁₁ Dialkyl Phthalate [25.4] NNO [6.9]
47F	None	Desmodur VK-5 [16.5]	8.0	Dibutyl Phthalate [43.2] C ₇ -C ₁₁ Dialkyl Phthalate [25.4] NNO [6.9]

¹ Kodaflex® DBP from Eastman Chemical Company² Palatinol® 711P from BASF Corporation³ NNO = Naphthenic Neutral Oil

EXAMPLE 48

The solutions in Example 47 were applied to 2000 denier, 1.5 tpi, polyester continuous filament yarn (AKZO Diolen Type 174S) as in Example 1 except solutions 47A and 47B were applied at a different rate sufficient to give a pick-up of 2.8 percent solids on the fiber. The treated fibers were heat treated as in Example 1. The treated fibers were tested as in Example 13 using the same carbon filled EPDM compound as used in Example 23 milled to a thickness of about 0.100 to 0.120 inches. The vulcanization conditions were 325°F for 30 minutes at 3200 PSI pressure. The results are shown in Table 15.

TABLE 15

Example	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
47A	3.67	4.54	Fiber to Rubber	40
47B	3.33	3.95	Fiber to Rubber	42
47C	2.09	2.86	Fiber to Rubber	43
47D	8.35	9.91	Rubber to Rubber (Thin)	37
47E	11.49	12.83	Rubber to Rubber	34
47F	13.33	15.14	Rubber to Rubber	29

5 The results in Tables 12, 13 and 15 support the results in
Tables 10 and 11 that an excess of isocyanate groups above that amount
of isocyanate groups that may react with the terminal hydroxyl groups of
the butadiene polymers, or isocyanate groups that may be involved in
such a reaction product by the reaction of another isocyanate group on the
same molecule is necessary to achieve the adhesion improvements of this
invention and that the addition of prepolymers, as are found in the prior
art, of isocyanate containing compounds with polybutadiene diols, alone
to an article to be bonded to rubber will not yield the adhesion improve-
ments contemplated by this invention.

EXAMPLE 49

15 The following adhesion samples were tested as in Example 13
using solutions 47A, 47B, 47C, 47D, 47E, and 47F with the following
differences. The compound used was the same carbon filled EPDM com-
pound as used in Example 23 milled to a thickness of about 0.100 to
0.120 inches. The vulcanization conditions were 325°F for 30 minutes
at 3200 PSI pressure. The untreated yarn (AKZO 174S polyester yarn) for
Example 48 was wound on the tape as in Example 13. Four 3 15/16" x
3 15/16" tape sections were used per adhesion press, along with four 1"
20 x 3 15/16" sections of aluminum foil. Four rubber compound sections
were cut, 3 15/16" x 3 15/16" each, per adhesion press. Each 3 15/16"
x 3 15/16" rubber section was weighed and then coated with a different
solution from Example 47 using a soft bristle paint brush. The brush was
cleaned with toluene after each solution application. After each rubber
25 section was coated, it was set aside for fifteen minutes and reweighed.
A different mold was used which consisted of a top and a bottom 10" x
10" flat aluminum plate (1/4" thick each) plus a middle 10" x 10" alumi-
num plate (3/4" thick) with four 4" x 4" cutouts and eight 4" x 4" plates

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(3/8" thick each) arranged and preheated to the specific compound vulcanization temperature in the hydraulic press. The samples were tested as in the general procedure in Example 13 with the noted exceptions. The data in Table 16 was obtained. This data shows that low adhesion is obtained with solutions 47A-47F when applied to the rubber instead of the yarn.

TABLE 16

10	Example	Weight of coating on the rubber section after 15 minutes (g)	Mean Load (lbf.)	Maximum Load (lbf.)	Failure Type	Pull Length (mm)
	47A	0.31	2.72	3.22	Fiber to Rubber	40
	47B	0.46	2.39	3.47	Fiber to Rubber	46
15	47C	0.23	0.75	1.51	Fiber to Rubber	35
	47D	0.25	2.50	3.39	Fiber to Rubber	44
	47E	0.21	1.68	2.02	Fiber to Rubber	44
	47F	0.25	2.87	3.96	Fiber to Rubber	41

EXAMPLE 50

20 The results of increased adhesion obtained by the combination of a large excess of isocyanate groups to terminal hydroxyl groups of polybutadiene of Examples 38 and 39 were explored in more detail with other terminal groups of butadiene polymers.

25 The hydroxyl terminated polybutadiene in Examples 50C and 50G was the previously used and described Poly bd R45HT Resin (Example 17) from Atochem North America. The carboxyl terminated polybutadiene in Examples 50D and 50H was compound number 525 from Scientific Polymer Products, Inc. This polymer had a number average molecular weight of approximately 4500, a weight average molecular weight by GPC of

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approximately 18,000, and a functionality of 1.9. The phenyl terminated polybutadiene in Examples 50E and 50I was compound number 443 from Scientific Polymer Products, Inc. This polymer had a number average molecular weight of approximately 3400, a weight average molecular weight by GPC of approximately 8,442, and 99% unsaturation (25% vinyl-1,2; 45% trans-1,4; 25% cis-1,4). The acrylate terminated polybutadiene in Examples 50F and 50J was Poly bd 300 Resin from Atochem North America, which is said to be the esterification reaction product of Poly bd R45HT with acrylic acid, with about one of the terminal hydroxyls remaining free and the other terminal group being the acrylate ester.

In Examples 50C through 50F, a molar ratio of about 50 to 1 or higher of NCO to terminal group for the various polybutadienes was used, giving a very large excess of polymethylene polyphenyl isocyanate (Desmodur VK-18). In Examples 50G through 50J, the molar ratio was much lower than in Example 50C through 50F, giving much less excess of polymethylene polyphenyl isocyanate (Desmodur VK-18). The amount of each different terminated butadiene polymer used in Table 17 was based on calculations of molar ratios of 50 to 1 and 2.5 to 1 moles of NCO to OH for the hydroxyl terminated polybutadiene in Example 50C. In the case of the other polymers in Table 17, the amounts used were based on maintaining the same amount of double bond equivalents for each different terminated polymer, as these were in the hydroxyl terminated polybutadiene (Poly bd R45HT) at the 50 to 1 molar ratio, since at the time it was thought that some of these polymers should not react with the isocyanate groups. However, as explained above, that may not be the case, so Table 17 is expressed in terms of molar ratio of NCO to known reactive group except in the case of the phenyl terminated polybutadiene, where the ratio is expressed in terms of NCO to phenyl group, assuming two phenyl groups, on each polymer molecule. The phenyl terminated

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polybutadiene actually was said to be made by an initiator system that should give two phenyl terminal groups with no reactive groups being present. However, it is possible that an unknown amount of hydroxyl groups were formed on the polymer molecules by oxidation of the polybutadiene double bonds. It was said that the polymer was several years old, contained no antioxidants, was exposed to the atmosphere and was manufactured for the purpose of oxidative polymerization.

The plasticizer dioctyl terephthalate (Kodaflex DOTP) completed the formulation. The yarns were treated as in Example 1 and tested for adhesion by the procedure of Example 13 using the carbon filled EPDM compound and the vulcanization conditions as in Example 38. The adhesion results for the varying ratios are shown in Table 17.

TABLE 17*

EXAM- PLE	POLYMETHYLENE POLYPHENYL ISOCYANATE (WT.%)	HYDROXYL TERM. POLY BUTADIENE (WT.%)	BUTADIENE POLYMER END GROUPS	MOLAR RATIO ISOCYANATE TO POLYMER TERMINAL GROUPS POLY 8D	DIOCTYL TEREPHTHALATE (WT.%)	TOLUENE (WT.%)	MEAN LOAD (lb./i.)	MAXIMUM LOAD (lb./i.)	FAILURE TYPE	PULL LENGTH (mm)
50A	17.5	0	NO POLYMER	INFINITY	82.5	0	3.50	4.53	FIBER TO RUBBER	43
50B	17.5	0	NO POLYMER	INFINITY	0	82.5	1.041	2.21	FIBER TO RUBBER	44
50C	17.5	3.25	HYDROXYL (POLY 8D R45HT)	49 TO 1	79.25	0	35.17	39.71	RUBBER TO RUBBER	28
50D	17.5	3.26	CARBOXYL (SPP #525)	86 TO 1	79.24	0	35.01	39.35	RUBBER TO RUBBER	27
50E	17.5	3.39	PHENYL (SPP #443)	66 TO 1	78.11	0	19.45	37.26	MIXED	37
50F	17.5	3.56	ACRYLATE (POLY 8D 300)	62 TO 1	78.84	0	30.34	40.59	RUBBER TO RUBBER	33
50G	4.58	16.17	HYDROXYL (POLY 8D R45HT)	2.56 TO 1	78.25	0	14.99	25.52	MIXED	39
50H	4.57	16.19	CARBOXYL (SPP #525)	5.03 TO 1	79.24	0	30.54	38.71	RUBBER TO RUBBER	31
50I	4.46	16.43	PHENYL (SPP #443)	3.47 TO 1	79.11	0	33.13	41.81	MIXED THIN	35
50J	4.32	16.74	ACRYLATE (POLY 8D 300)	1.36 TO 1	78.94	0	11.97	26.62	MIXED THIN	40

* wt% values, in Table 17, are given to an accuracy of ± 0.02 .

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The data in Table 17 shows that polyunsaturated polymers with phenyl, hydroxyl, carboxyl and acrylate terminal groups can provide yarns which exhibit high adhesion to the EPDM elastomer.

5 In Table 17, the molar ratios of isocyanate to polymer terminal group were calculated using Desmodur VK-18 (from Example 9) with a 31.5% isocyanate content as in Example 38. In the case of carboxyl, phenyl, and acrylated terminated polybutadienes, the following formula was used to calculate equivalent weight (EW): $EW = \text{Molecular Weight (Mn)} / \text{Functionality}$. A functionality of 2.0 was used for the phenyl-
10 terminated polybutadiene, and a functionality of 1.0 was used for the acrylated polybutadiene.

EXAMPLE 51

Example 50 was further expanded to demonstrate the effect of different polymers of butadiene with various terminal end groups. Poly-
15 methylene polyphenyl isocyanate as Desmodur VKS-18 was used at 17.2% in each of the solutions in Example 51. The plasticizers dioctyl adipate (DOA as Kodaflex DOA from Eastman Chemical Company) and C₇-C₁₁ dialkyl phthalate (Palatinol® 711P, Palatinol® is a trademark of BASF Corporation) completed the formulation. The amount of Palatinol
20 711P was 25.0% in each of the treating solutions while the amount of Kodaflex DOA varied as indicated in Table 18. The solutions were made by making two premixes. Premix "A" consisted of the specified amount of the designated isocyanate added to the specified amount of Palatinol 711P or the plasticizer(s) which replaced it in that particular experiment
25 and stirring with a magnetic stirrer until a homogeneous solution resulted. Premix "B" was formed by adding the Kodaflex PA-6 to the hydroxyl terminated polybutadiene and then adding the Kodaflex DOA, or the

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plasticizers which replaced it in that particular experiment. The mixture was then stirred with a magnetic stirrer until a homogeneous solution was obtained. The solutions were then mixed and stirred using the magnetic stirrer and applied to yarn as in Example 1.

5 The Poly bd R20LM Resin from Atochem North America in Example 51C has been described earlier. The Poly bd 605 Resin from Atochem North America in Example 51D is an epoxidized polybutadiene diol with an epoxy equivalent weight of about 260, an oxirane oxygen content of about 6.5%, a hydroxyl value of about 2.7 meq/g, a viscosity of about
10 250 P at 25°C, a microstructure of 15% cis, 55% trans and 30% vinyl and a number average molecular weight of approximately 1400. The Poly bd 600 Resin from Atochem North America in Example 51E had an epoxy equivalent weight of about 460, an oxirane oxygen content of about 3.5%, a viscosity of about 55 P at 25°C, a microstructure of 15% cis,
15 55% trans and 30% vinyl and a number average molecular weight of approximately 1400. The carboxyl terminated polybutadiene in Example 51F was compound number 524 from Scientific Polymer Products, Inc. This polymer had a number average molecular weight of approximately 4000, a weight average molecular weight by GPC of approximately
20 17,000, and a functionality of 1.9. The carboxyl terminated polybutadiene in Example 51G was compound number 525 from Scientific Polymer Products, Inc., described in Example 50. The carboxyl terminated polybutadiene in Example 51H was compound number 526 from Scientific Polymer Products, Inc. This polymer had a number average molecular
25 weight of approximately 4000, a weight average molecular weight by GPC of approximately 16,000 and a functionality of 1.9. The acrylate terminated polybutadiene in Example 51I was Poly bd 300 Resin, described in Example 50. The vinyl (acrylate) terminated acrylonitrile/butadiene copolymer in Example 51J was compound number 516 from

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Scientific Polymer Products, Inc. This polymer had a number average molecular weight of approximately 2000, an acrylonitrile content of about 16.2%, a vinyl equivalent weight of about 1,100, a Brookfield viscosity of about 250,000 cps at 27°C and an acrylic vinyl content of about 3.8% and a functionality of 1.9. The vinyl (acrylate) terminated acrylonitrile/butadiene copolymer in Example 51K was compound number 522 from Scientific Polymer Products, Inc. This polymer had a number average molecular weight of approximately 2500, an acrylonitrile content of about 16.5%, a vinyl equivalent weight of about 1,400, a Brookfield viscosity of about 225,000 cps at 27°C and an acrylic vinyl content of about 3.0%. The solutions were made up as in Example 38 and applied to yarn as in Example 1 but a 3.3 TPI polyester was used. The treated yarns were tested for adhesion by the procedure of Example 13 using a different carbon filled EPDM compound used in commercial hoses which had been milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 315°F for 45 minutes at 3200 psi. The adhesion results for the varying ratios are shown in Table 18.

TABLE 18

EXAM- PLE	UNSATURATED POLYMER	TERMINAL GROUPS AND OTHER REACTIVE GROUPS	DIOCTYL ADIPATE (WT.%)	POLYMER RATED	PERCENT UNSATU RATED	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
51A	NO POLYMER	NA	57.80	NA	NA	1.15	2.02	FIBER TO RUBBER	44
51B	POLYBUTADIENE	HYDROXYL	53.79	4.01	4.01	12.66	21.32	MIXED	32
51C	POLYBUTADIENE	HYDROXYL	53.73	4.07	4.07	11.05	18.36	MIXED	33
51D	POLYBUTADIENE	HYDROXYL AND EPOXY	53.38	4.41	4.41	5.41	6.45	FIBER TO RUBBER	38
51E	POLYBUTADIENE	HYDROXYL AND EPOXY	53.59	4.21	4.21	7.39	8.82	FIBER TO RUBBER	36
51F	POLYBUTADIENE	CARBOXYL	53.77	4.04	4.04	5.83	7.38	FIBER TO RUBBER	39
51G	POLYBUTADIENE	CARBOXYL	53.77	4.04	4.04	6.66	8.03	FIBER TO RUBBER	40
51H	POLYBUTADIENE	CARBOXYL	53.77	4.03	4.03	6.18	7.34	FIBER TO RUBBER	41
51I	POLYBUTADIENE	ACRYLATE AND HYDROXYL	53.42	4.39	4.39	8.51	10.81	MIXED/FIBER TO RUBBER	36
51J	ACRYLONITRILE/ BUTADIENE	ACRYLATE AND HYDROXYL	52.85	4.95	4.95	9.70	11.87	MIXED/FIBER TO RUBBER	35
51K	ACRYLONITRILE/ BUTADIENE	ACRYLATE AND HYDROXYL	52.89	4.91	4.91	10.18	12.42	MIXED	34

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EXAMPLE 52

The three basic components of this invention - isocyanate, plasticizer, and polyunsaturated polymer - were applied in various combinations in two step applications versus a one step application. This example indicates that better adhesion is obtained if the isocyanate is applied with the plasticizer, that the isocyanate and the potentially reactive hydroxyl terminated polybutadiene do not have to be applied at the same time and that there is no apparent benefit in a two step application versus a one step application. Each of the solutions in each application was made by the general procedure of Example 38. Toluene was added to each solution in each application to compensate for the 12% pickup to maintain the proper amount of each component on the yarn. Dioctyl terephthalate (Kodaflex DOTP) was the plasticizer used. The treated yarns were evaluated for adhesion properties by the procedure of Example 13 using a specially formulated carbon filled EPDM compound which had been milled to a thickness of approximately 0.100 to 0.120 inches. The vulcanization conditions were 330°F for 30 minutes at 3200 psi. The results are shown in Table 19.

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TABLE 19*

EXAMPLE	FIRST TREATMENT	SECOND TREATMENT	TOTAL AMOUNT OF DESMODUR VK-18	TOTAL AMOUNT OF POLY BD R45HT	TOTAL AMOUNT OF PLASTICIZER	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
52A	Isocyanate Only	OH Term. Poly BD Only	17.5	3.25	NONE	4.31	5.23	FIBER TO RUBBER	39
52B	Isocyanate Only	OH Term. Poly BD & Plasticizer	17.5	3.25	79.25	1.84	2.21	FIBER TO RUBBER	43
52C	Isocyanate Only	Isocyanate & OH Term. Poly BD & Plasticizer	35.0	3.25	61.75	13.67	19.90	MIXED	25
52D	1/2 Isocyanate Only	1/2 Isocyanate & OH Term. Poly BD & Plasticizer	17.5	3.25	79.25	11.10	14.48	MIXED	29
52E	Isocyanate & OH Term. Poly BD	Plasticizer only	17.5	3.25	79.25	2.59	3.17	FIBER TO RUBBER	42
52F	Isocyanate & OH Term. Poly BD	Isocyanate & Plasticizer Only	35.0	3.25	61.75	2.51	3.02	FIBER TO RUBBER	41
52G	1/2 Isocyanate & OH Term. Poly BD	1/2 Isocyanate & Plasticizer Only	17.5	3.25	79.25	2.94	3.65	FIBER TO RUBBER	41
52H	Isocyanate & OH Term. Poly BD & Plasticizer	Isocyanate Only	35.0	3.25	61.75	9.32	11.35	MIXED	31
52I	Isocyanate & Plasticizer Only	OH Term. Poly bd Only	17.5	3.25	79.25	10.53	12.79	MIXED	30
52J	Isocyanate & Plasticizer Only	OH Term. Poly bd & Plasticizer	17.5	3.25	79.25	7.05	8.16	FIBER TO RUBBER	36
52K	Isocyanate & OH Term. Poly BD & Plasticizer	NONE	17.5	3.25	79.25	15.08	19.42	MIXED	22
52L	Isocyanate & OH Term. Poly BD & Plasticizer	NONE	35.0	3.25	61.75	10.84	13.36	MIXED	28

* wt% values, in Table 19, are given to an accuracy of ± 0.02 .

EXAMPLE 53

The treated yarns from Example 52 were also evaluated for adhesion by the same procedure as used in Example 52 with the same chlorobutyl compound under the same vulcanization conditions as in Example 37.

5 The results are shown in Table 20.

Tables 19 and 20 show that there is no advantage in adhesion in applying an isocyanate pretreatment to the polyester yarn, as is done with RFL treatments, with the adhesion system of this invention (Examples C and D versus Examples K and L). The results in Tables 19 and 20 also
10 indicate that the isocyanate should be dissolved or dispersed in the plasticizer when it is applied to the article as opposed to separate applications and preferably with or before the third component (polyunsaturated polymer) in order to obtain the adhesion improvements contemplated by this invention (Examples I and J versus Examples A, B, E,
15 F, G and H) and that the addition of all three components in the same solution or dispersion is the best way to achieve the adhesion improvements of this invention.

TABLE 20*

EXAM- PLE	FIRST TREATMENT	SECOND TREATMENT	TOTAL AMOUNT OF DESMODUR VK-18	TOTAL AMOUNT OF POLY BD R46HT	TOTAL AMOUNT OF PLASTICIZER	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
53A	Isocyanate Only	OH Term. Poly BD Only	17.50	3.25	NONE	7.14	11.55	MIXED	41
53B	Isocyanate Only	OH Term. Poly BD & Plasticizer	17.50	3.25	79.25	5.57	7.02	MIXED (THIN)	41
53C	Isocyanate Only	Isocyanate & OH Term. Poly BD & Plasticizer	35.00	3.25	61.75	14.91	16.16	RUBBER TO RUBBER	32
53D	1/2 Isocyanate Only	1/2 Isocyanate & OH Term. Poly BD & Plasticizer	17.50	3.25	79.25	14.55	15.82	RUBBER TO RUBBER	32
53E	Isocyanate & OH Term. Poly BD	Plasticizer only	17.50	3.25	79.25	5.27	6.24	MIXED	41
53F	Isocyanate & OH Term. Poly BD	Isocyanate & Plasticizer Only	35.00	3.25	61.75	13.82	15.63	MIXED	35
53G	1/2 Isocyanate & OH Term. Poly BD	1/2 Isocyanate & Plasticizer Only	17.50	3.25	79.25	7.51	10.01	MIXED	39
53H	Isocyanate & OH Term. Poly BD & Plasticizer	Isocyanate Only	35.00	3.25	61.75	13.06	14.79	RUBBER TO RUBBER	35
53I	Isocyanate & Plasticizer Only	OH Term. Poly bd Only	17.50	3.25	79.25	14.13	17.76	RUBBER TO RUBBER	34
53J	Isocyanate & Plasticizer Only	OH Term. Poly bd & Plasticizer	17.50	3.25	79.25	14.08	17.23	RUBBER TO RUBBER	34
53K	Isocyanate & OH Term. Poly BD & Plasticizer	NONE	17.50	3.25	79.25	14.89	16.49	RUBBER TO RUBBER	34
53L	Isocyanate & OH Term. Poly BD & Plasticizer	NONE	35.00	3.25	61.75	12.32	13.62	RUBBER TO RUBBER	35

* wt% values, in Table 20, are given to an accuracy of ± 0.02 .

EXAMPLE 54

The effect of the isocyanate groups on the treated yarn was studied by exposing treated yarn to three different moisture conditions. Isocyanate groups are quite reactive to water, so varying moisture conditions should give some indication of the role that the isocyanate group plays in regard to adhesion properties and in interaction with the other components. Yarn was treated with four different formulations containing some or all of the basic components of this invention. The four different treatments were isocyanate only, isocyanate plus plasticizer, isocyanate plus hydroxyl terminated polybutadiene and isocyanate plus hydroxyl terminated polybutadiene plus plasticizer. Each of these four different yarns were exposed to three different moisture conditions.

The first moisture condition was to minimize exposure of the treated yarns to water by immediately securing the package of wound yarn, after treatment with its particular formulation, in a Polyethylene Zip-Lock bag, flushed with nitrogen and sealed. The package of treated yarn was removed from the bag and immediately placed in the oven for the heat treatment as in Example 1. After removal from the oven, the package was allowed to cool for one hour and then returned to the bag. The bag was flushed with nitrogen and sealed. The package of treated yarn was not removed from the sealed bag until it was tested as in Example 13.

The second moisture condition was, immediately after the initial treatment with the specific formulation as in Example 1, to repeat the treating step with water as the treating solution. The rewound package was then heat treated as in Example 1.

The third moisture condition was to follow Example 1 with each of the four different formulations except to retreat each treated yarn as in Example 1 with water approximately eight hours after completing the heat cycle as in Example 1. Each of the twelve different treated yarns were

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tested for adhesion by the procedure of Example 13 using the same EPDM rubber compound and vulcanization conditions as used in Example 14 except that the rubber compound was milled to a thickness of 0.100 to 0.120 inches. The results are shown in Table 21.

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TABLE 21

EXAMPLE	COMPOSITION	POST TREATMENT TREATED PACKAGE HANDLING	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
54B1	Isocyanate Only	Under nitrogen before and after heat treatment	2.39	3.43	Mixed	44
54C1	Isocyanate Only	Run through water before heat treatment	2.13	3.07	Fiber to Rubber	49
54D1	Isocyanate Only	Run through water after heat treatment	1.45	4.12	Fiber to Rubber	33
54B2	Isocyanate and Plasticizer	Under nitrogen before and after heat treatment	4.49	5.61	Fiber to Rubber	44
54C2	Isocyanate and Plasticizer	Run through water before heat treatment	9.77	13.00	Rubber to Rubber	39
54D2	Isocyanate and Plasticizer	Run through water after heat treatment	5.60	10.24	Fiber to Rubber	42
54B3	Isocyanate and Hydroxyl Terminated Polybutadiene	Under nitrogen before and after heat treatment	11.73	13.17	Rubber to Rubber	35
54C3	Isocyanate and Hydroxyl Terminated Polybutadiene	Run through water before heat treatment	12.44	13.76	Rubber to Rubber	34
54D3	Isocyanate and Hydroxyl Terminated Polybutadiene	Run through water after heat treatment	9.95	12.42	Rubber to Rubber	38
54B4	Isocyanate and Hydroxyl Terminated Polybutadiene and Plasticizer	Under nitrogen before and after heat treatment	13.44	15.35	Rubber to Rubber	30
54C4	Isocyanate and Hydroxyl Terminated Polybutadiene and Plasticizer	Run through water before heat treatment	13.78	14.87	Rubber to Rubber	32
54D4	Isocyanate and Hydroxyl Terminated Polybutadiene and Plasticizer	Run through water after heat treatment	14.13	15.59	Rubber to Rubber	34

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The data in Table 21 indicates that water applied to the yarn containing the components of this invention, either applied before or after a heat treatment, has no detrimental effect on adhesion to rubber. This result further indicates that the adhesion improvement, which appears to require excess isocyanate groups applied to the yarn (Examples 38 and 39) may not be necessarily effected by the isocyanate groups themselves but possibly by some reaction product of the isocyanate groups, such as with water from the ambient air.

EXAMPLES 55, 56, 57, 58, 59, 60, 61, 62, 63 and 64

Tables 22, 23, 24, 25, 26, 27, 28, 29, 30 and 31 contain data from Examples 55-64, respectively. Examples 55-64 demonstrate the invention with different combinations of different isocyanates, different plasticizers, polybutadiene diol, and poly(2,2,4-trimethyl-1,3-pentanediol maleate) on different fibers. The treating solutions were made by making two premixes as in Example 51. In Examples 58-64, the two solutions were metered separately by two peristaltic pumps at the proper ratio into a pan containing a kiss roll. The filament yarns were then passed over the kiss roll, which was geared to give a pickup of 11.5% and wound by direct drive winders on tubes as in Example 1 except that full 8" diameter packages were made. The wound tubes were then heat treated as in Example 1. The solution in the pan was replenished as necessary by the metering pumps, which were activated by a float device. The pickup was determined by comparing the weights of the average of three each of 30 meter skeins of freshly treated yarn with dry untreated yarn. The percent pick up was calculated by the formula: 100 times (Average Treated Weight minus Average Untreated Weight) divided by (Average Untreated Weight).

In Examples 55D, 55K and 56F, the Desmorapid LA was added to the "B" solution after all of the other components were mixed. In

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Example 55F, the KP-140[®] (Tri-butoxy ethyl Phosphate) (KP-140[®] is a trademark of FMC) replaced Palatinol 711P in the mixing procedure. In Example 55G, the Plasthall[®] DIBA diisobutyl adipate (Plasthall[®] is a trademark of The C.P. Hall Co.) replaced Palatinol 711P while in Example 55I, the Kodaflex DBP replaced Kodaflex DOA.

Example 55J had Cymel[®] 303 and Cycat[®] 600 added to Premix B. Cymel[®] and Cycat[®] are registered trademarks of American Cyanamid Company. Cymel[®] 303 is hexamethylmelamine, and is a crosslinking agent for polymers containign carboxyl, hydroxyl or amide groups. Cycat[®] 600 is an aromatic sulfonic acid catalyst for Cymel[®] 303.

Example 55 (Table 22) used Polyvinyl Alcohol 1200 Denier 2.5 TPI Mewlon filament yarn from Unitika, Japan. The compound used was a carbon filled EPDM used in commercial hoses. This compound had been milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 320°F for 25 minutes at 3200 psi.

Example 56 (Table 23) used Nomex 1200 Denier 2.0 TPI filament yarn from Du Pont Fibers. The compound used was the same carbon filled EPDM with the same vulcanization conditions used in Example 54. This compound had been milled to a thickness of 0.100 to 0.120.

Example 57 (Table 24) used 840/3 5.0 TPI Nylon filament yarn from Akzo Fibers. The compound used was a carbon filled chlorinated sulfonated polyethylene (Hypalon) used in commercial power steering hoses. This compound had been milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 315°F for 30 minutes at 3200 psi.

Examples 58, 60, 61, 62 (Tables 25, 27, 28 and 29) used 1000/1 1.5 TPI Polyester Filament yarn type 174S from Akzo Fibers. Examples 59 and 63 (Tables 26 and 30) used 2000/1 1.5 TPI Polyester Filament yarn type 174S from Akzo Fibers. Example 64, Table 31, used 1300/1 3.3 TPI Polyester filament yarn type 174S, as above. In Examples

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58, 60 and 61, the yarns were wound from the 8" diameter package from the treating step onto 5 1/4" diameter cones using a Leesona Model 50 winder. In Examples 59, 62 and 63, the yarns were wound from the 8" diameter package from the treating step after heat treatment onto 7" diameter cones using a Leesona Model 50 winder. In Examples 64A, B, C and E (Table 31), the yarns were wound from three 8" diameter treater packages from the treating step onto one 5" long tube (two ends up) using a Leesona Model 50 winder for subsequent use on a braider. The three ends (two separate yarns) would then be pulled off of the braider package together for incorporation into a hose. In each of the examples in Table 31, one of these two ends, or yarns, was tested as described in the Table. The yarn in Example 64D was wound from one 8" diameter treater package onto one 5" long braider tube or package (one end up).

All of the treated yarns as described above were tested for adhesion by the procedure of Example 13. The rubber compound and vulcanization conditions used in Example 58 were exactly the same as in Example 21. The rubber compound used in Example 59 was a carbon filled chlorobutyl rubber which had been milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 320°F for 25 minutes. The rubber compound used in Example 60 was a carbon filled nitrile/PVC (polyvinyl chloride) blend rubber which had been milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 325°F for 30 minutes. The rubber compound used in Example 61 was a carbon filled neoprene rubber which had been milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 325°F for 30 minutes. The rubber compound used in Example 62 was a carbon filled chlorobutyl rubber which had been milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 310°F for 40 minutes. The rubber compound used in Example 63 was a carbon filled natural rubber which had

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5 been milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 350°F for 5 minutes. The rubber compound and vulcanization conditions used in Example 64 were exactly the same as for Example 23. The data in Tables 55-64 demonstrates that various yarns treated with adhesion systems of this invention which contain both hydroxy terminated polybutadienes and polymaleate esters show high adhesion to many rubbers and elastomers and when applied to different polymeric materials.

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TABLE 22

Exempl	ISOCYANATE (% BY WT.)	HYDROXYL TERM. POLY BUTADIENE (% BY WT.)	POLY MALEATE ESTER (% BY WT.)	PLASTICIZER (% BY WT.)	OTHER	MEAN LOAD (lb./i.)	MAXIMUM LOAD (lb./i.)	FAILURE TYPE	PULL LENGTH (mm)
SSA	Non-RFL Commercial Treatment on PVA Yarn				None	3.24	4.08	Fiber to Rubber	44
SSB	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From Kodaflex [®] PA-6 [2.5]	Kodaflex DOA [43.3] Pelathol 711P [25.0] DOTP ¹ [10.0]	None	33.16	42.02	Rubber to Rubber	27
SSC	Desmodur VKS-18 [35.0]	Poly bd R45HT [2.0]	From Kodaflex PA- 6 [2.5]	Kodaflex DOA [30.5] Pelathol 711P [20.0] DOTP ¹ [10.0]	None	33.82	42.70	Rubber to Rubber	27
SSD	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From Kodaflex PA- 6 [2.5]	Kodaflex DOA [43.1] Pelathol 711P [25.0] DOTP ¹ [10.0]	Desmoreplid LA Iso- cyanate catalyst from Miles, Inc. [0.2]	33.80	38.71	Rubber to Rubber	28
SSE	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	From Kodaflex PA- 6 [5.0]	Kodaflex DOP [37.8] DOTP ¹ [20.0] Pelathol 711P [15.0]	None	23.47	31.25	Mixed	35
SSF	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From Kodaflex PA- 6 [2.5]	Kodaflex DOA [43.3] KP-140 [®] [25.0] DOTP ¹ [10.0]	None	24.43	35.87	Mixed	30
SSG	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From Kodaflex PA- 6 [2.5]	Kodaflex DOA [43.3] Plasthall DIBA [25.0] DOTP ¹ [10.0]	None	20.31	34.53	Rubber to Rubber	32
SSH	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [5.0]	None	Kodaflex DOA [52.8] Pelathol 711P [25.0]	None	32.14	39.93	Rubber to Rubber	28
SSI	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From Kodaflex PA- 6 [2.5]	Kodaflex DBP [43.3] Pelathol 711P [25.0] DOTP ¹ [10.0]	None	14.18	22.92	Mixed	38
SSJ	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From Kodaflex PA-6 [2.5]	Kodaflex DOA [37.8] Pelathol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	Cymal [®] 303 [5.0] Cycat [®] 600 [0.5]	37.05	46.41	Rubber to Rubber	24
SSK	Desmodur VKS-18 [17.2]	Poly bd 605 [2.0]	From Kodaflex PA-6 [2.5]	Kodaflex DOA [43.1] Pelathol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	Desmoreplid LA [0.2]	10.25	12.92	Mixed	41

¹ DOTP from Kodaflex PA-6

TABLE 23

Exemple	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	OTHER	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
56A	Non-RFL Commercial Treatment on Nomex Yarn					7.12	8.29	Mixed	41
56B	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex® DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	None	12.80	14.61	Rubber to Rubber	34
56C	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	NONE	Kodaflex DOA [52.8] Palatinol 711P [25.0]	None	12.99	14.36	Rubber to Rubber	36
56D	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	From PA-6 [5.0]	Kodaflex DOA [27.8] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	None	14.28	15.98	Rubber to Rubber	34
56E	Desmodur VK-5 [17.2]	Poly bd R45HT [5.0]	From PA-6 [5.0]	Kodaflex DOA [27.8] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	None	13.55	15.38	Rubber to Rubber	32
56F	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	From PA-6 [5.0]	Kodaflex DOA [27.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	Desmoreplid LA Isocyanate catalyst from Miles, Inc. [0.5]	13.35	15.08	Rubber to Rubber	34

TABLE 24

Example	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
57A	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex® DOA [34.2] Palatinol® 711P [34.1] Dioctyl Terephthalate from Kodaflex PA-6 [10.0]	9.37	11.93	Rubber to Rubber	41
57B	Desmodur VK-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [34.2] Palatinol 711P [34.1] Dioctyl Terephthalate from Kodaflex PA-6 [10.0]	9.52	10.89	Rubber to Rubber-thin	41
57C	Desmodur VK-5 [15.8]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [34.9] Palatinol 711P [34.8] Dioctyl Terephthalate from Kodaflex PA-6 [10.0]	10.05	11.35	Rubber to Rubber-thin	41
57D	Desmodur VKS-18 [21.5]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [32.0] Palatinol 711P [32.0] Dioctyl Terephthalate from Kodaflex PA-6 [10.0]	7.83	9.99	Rubber to Rubber	40
57E	Desmodur VKS-18 [17.2]	Poly bd 605 [2.0]	From PA-6 [2.5]	Kodaflex DOA [34.2] Palatinol 711P [34.1] Dioctyl Terephthalate from Kodaflex PA-6 [10.0]	7.83	11.35	Rubber to Rubber	40
57F	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [34.1] Palatinol 711P [34.1] Dioctyl Terephthalate from Kodaflex PA-6 [10.0] and Desmorepid LA [0.1] as catalyst	8.52	10.87	Rubber to Rubber-thin	41
57G	RFL Treated Nylon				6.73	11.08	Rubber to Rubber	42
57H	Commercial Non-RFL Nylon Treatment				2.92	3.40	Fiber to Rubber	45

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TABLE 25

Example	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lb.f.)	MAXIMUM LOAD (lb.f.)	FAILURE TYPE	PULL LENGTH (mm)
58A	Non-RFL	Commercial	Isocyanate	Treated Yarn	9.32	10.93	Mixed-thin	40
58B	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatinal 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	14.62	16.04	Rubber to Rubber	36
58C	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex [®] DOA [43.3] Palatinal 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	13.08	15.30	Rubber to Rubber	33
58D	Desmodur VKS-18 [17.2]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [28.8] Palatinal 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	14.68	16.36	Rubber to Rubber	36
58E	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [68.3] DOTP from Kodaflex PA-6 [10.0]	13.66	15.42	Rubber to Rubber	33
58F	Desmodur VKS-18 [17.2]	None	From PA-6 [2.5]	Kodaflex DOA [45.3] Palatinal 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	12.75	14.18	Rubber to Rubber	36
58G	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [5.0]	Kodaflex DOA [30.8] Palatinal 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	12.06	13.69	Rubber to Rubber	35
58H	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	From PA-6 [2.5]	Kodaflex DOA [40.3] Palatinal 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	13.11	14.48	Rubber to Rubber	33
58I	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Kodaflex TXIB [25.0] DOTP from Kodaflex PA-6 [10.0]	12.87	14.42	Rubber to Rubber	33
58J	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	None	Kodaflex DOA [55.8] Palatinal 711P [25.0]	13.21	14.84	Rubber to Rubber	33

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TABLE 2B

Exemple	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lb.)	MAXIMUM LOAD (lb.)	FAILURE TYPE	PULL LENGTH (mm)
59A	Commercial Non-RFL	Treated	Yarn		4.67	5.42	Mixed-Thin	43
59B	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	None	Kodaflex DOA [77.8]	13.50	14.94	Rubber to Rubber-Thin	39
59C	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [5.0]	None	Kodaflex DOA [52.8] Palatinol 711P [25.0]	11.39	12.98	Rubber to Rubber-Thin	39
59D	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	10.98	12.98	Mixed-Thin	39
59E	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [68.3] DOTP from Kodaflex PA-6 [10.0]	9.67	11.80	Mixed-Thin	40
59F	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Kodaflex TX18 [25.0] DOTP from Kodaflex PA-6 [10.0]	8.29	9.81	Mixed-Thin	40
59G	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 71 [25.0] DOTP from Kodaflex PA-6 [10.0]	8.26	10.02	Mixed-Thin	40
59H	Desmodur VKS-18 [17.2]	None	From PA-6 [2.5]	Kodaflex DOA [45.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	7.25	8.73	Mixed-Thin	41
59I	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	None	Kodaflex DOA [55.8] Palatinol 711P [25.0]	9.79	11.89	Mixed-Thin	41
59J	Desmodur VKS-18 [35.0]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [25.5] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	11.99	13.16	Rubber to Rubber-Thin	39
59K	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DBP [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	7.03	8.22	Mixed-Thin	42

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TABLE 27

Example	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
60A		Commercial	Non-RFL	Treated Yarn	5.81	7.03	Mixed	42
60B	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	18.97	19.89	Rubber to Rubber	35
60C	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	17.08	19.80	Rubber to Rubber	35
60D	Desmodur VKS-18 [17.2]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [28.8] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	18.79	18.97	Mixed	35
60E	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [68.3] DOTP from Kodaflex PA-6 [10.0]	14.69	17.82	Mixed	37
60F	Desmodur VKS-18 [17.2]	None	From PA-6 [2.5]	Kodaflex DOA [45.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	11.43	14.36	Mixed	37
60G	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [5.0]	Kodaflex DOA [30.8] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	18.24	18.66	Rubber to Rubber	35
60H	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	From PA-6 [2.5]	Kodaflex DOA [40.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	14.16	17.82	Mixed	37
60I	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Kodaflex TXIB [25.0] DOTP from Kodaflex PA-6 [10.0]	13.55	17.07	Mixed	37
60J	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	NONE	Kodaflex DOA [55.8] Palatinol 711P [25.0]	15.03	17.70	Rubber to Rubber	37

TABLE 28

Example	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
61A	Non-RFL	Commercial	Treated	Yarn	8.10	10.10	Mixed	39
61B	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	10.67	12.62	Rubber to Rubber	38
61C	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	12.30	14.32	Rubber to Rubber	38
61D	Desmodur VKS-18 [17.2]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [28.8] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	9.80	12.18	Mixed	37
61E	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [88.3] DOTP from Kodaflex PA-6 [10.0]	10.72	13.19	Rubber to Rubber	36
61F	Desmodur VKS-18 [17.2]	None	From PA-6 [2.5]	Kodaflex DOA [45.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	9.49	12.37	Rubber to Rubber	37
61G	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [5.0]	Kodaflex DOA [30.8] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	10.09	11.77	Rubber to Rubber	38
61H	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	From PA-6 [2.5]	Kodaflex DOA [40.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	10.69	12.37	Rubber to Rubber	39
61I	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Kodaflex TXIB [25.0] DOTP from Kodaflex PA-6 [10.0]	9.97	11.53	Mixed	39
61J	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	NONE	Kodaflex DOA [55.8] Palatinol 711P [25.0]	8.71	10.24	Mixed	39

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TABLE 29

Example	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
62A	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From Kodaflex PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	10.37	12.28	Rubber to Rubber thin	38
62B	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Plasthall DIBA [25.0] DOTP from Kodaflex PA-6 [10.0]	10.20	12.01	Rubber to Rubber	38
62C	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DBP [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	10.64	13.05	Mixed	38
62D	Desmodur VKS-18 [17.2]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [28.8] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	10.25	11.94	Rubber to Rubber	38
62E	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.0] DOTP from Kodaflex PA-6 [10.0] Palatinol 711P [25.0] Desmorepid LA [0.3]	11.15	12.67	Rubber to Rubber	38
62F	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [68.3] DOTP from Kodaflex PA-6 [10.0]	9.90	12.15	Rubber to Rubber	38
62G	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [5.0]	Kodaflex DOA [30.8] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [20.0]	10.20	12.15	Rubber to Rubber	37
62H	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	From PA-6 [2.5]	Kodaflex DOA [40.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	10.83	12.49	Rubber to Rubber	37
62I	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [35.5], Palatinol 711P [17.6] and NNO [15.2] DOTP from Kodaflex PA-6 [10.0]	10.63	13.00	Rubber to Rubber	38

NNO = naphthenic neutral oil

TABLE 30

EXAMPLE	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
63A1	Non-RFL	Commercial	Treated Yarn	Source A	7.28	8.55	Fiber to Rubber	40
63A2	Non-RFL	Commercial	Treated Yarn	Source B	7.33	8.16	Fiber to Rubber	39
63B	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	16.48	24.06	Mixed	28
63C	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	NONE	Kodaflex DBP [52.8] Palatinol 711P [25.0]	17.65	25.50	Mixed	26
63D	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DBP [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	15.73	20.63	Mixed	33
63E	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Plesthall DIBA [25.0] DOTP from Kodaflex PA-6 [10.0]	9.29	12.21	Mixed	30
63F	Desmodur VKS-18 [17.2]	Poly bd R45HT [5.0]	NONE	Kodaflex DOA [77.8]	14.60	20.78	Mixed	31
63G	Desmodur VKS-18 [35.0]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [25.5] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	20.60	28.29	Mixed	25
63H	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [35.5] Palatinol 711P [17.6] DOTP from Kodaflex PA-6 [10.0] Naphthenic neutral oil [15.2]	20.68	29.10	Mixed	26
63I	Desmodur VKS-18 [8.6] Desmodur VK-5 [8.6]	Poly bd R45HT [5.0]	From PA-6 [5.0]	Kodaflex DOA [52.8] DOTP from Kodaflex PA-6 [20.0]	18.64	28.82	Mixed	28
63J	Desmodur VKS-18 [17.2]	NONE	From PA-6 [2.5]	Kodaflex DOA [45.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	13.36	15.12	Mixed	36
63K	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] DOTP from Kodaflex PA-6 [10.0] KP-140 [®] [25.0]	15.13	17.31	Mixed	32

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TABLE 31

EXAMPLE	ISOCYANATE	PERCENT OH TERM. POLY BUTADIENE	POLY MALEATE ESTER	PLASTICIZER TYPE & AMOUNT	YARN TREATED	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
64A	Commercial	Non-RFL	Treated Yarn		One End of Two Ends Up	4.97	6.45	Mixed	44
64B	Desmodur VK-5 [16.4%]	5.0	0	Diethyl Adipate (DOA) [78.6%]	One End of Two Ends Up	10.65	11.95	Rubber to Rubber	35
64C	Desmodur VK-5 [16.4%]	2.0	From Kodaflex PA-6 [2.5%]	DOA [44.1%] Pelatinal 711P [25.0%] DOTP from Kodaflex PA-6 [10.0%]	First End of Two Ends Up	11.03	12.09	Rubber to Rubber	36
64D	Desmodur VK-5 [16.4%]	2.0	From Kodaflex PA-6 [2.5%]	As Example 64C	Second End of Two Ends Up	12.22	14.00	Rubber to Rubber	36
64E	Desmodur VK-5 [16.4%]	2.0	From Kodaflex PA-6 [2.5%]	As Example 64C	One End of One End Up	11.96	13.02	Rubber to Rubber	34

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EXAMPLE 65

The amounts of each of the three components of this invention on the fiber were varied by varying the amount of each component in the treating solution and by varying the pick-up of the treating solution on the yarn. Akzo Type 174S 1000/1 1.5 TPI polyester yarn was treated by the procedure of Example 19. The treated yarns were tested for adhesion by the procedure of Example 13. The rubber compound was the same carbon filled EPDM as used in Example 15 with the same vulcanization conditions. High adhesion of the treated yarns to the carbon filled EPDM is obtained for the various formulations and amounts of the adhesion system on the yarn. The results are shown in Table 32.

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TABLE 32

EXAMPLE	ISOCYANATE (% BY WEIGHT ON FIBER)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT ON FIBER)	POLY MALEATE ESTER (% BY WEIGHT ON FIBER)	PLASTICIZER (% BY WEIGHT ON FIBER)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
65A	Desmodur VKS-18 [2.10]	Poly bd R45HT [0.24]	From PA-6 [0.30]	Kodaflex DOA [8.16] DOTP from Kodaflex PA-6 [1.20]	29.89	33.85	Rubber to Rubber	29
65B	Desmodur VKS-18 [4.20]	Poly bd R45HT [0.48]	From PA-6 [0.60]	Kodaflex DOA [4.32] DOTP from Kodaflex PA-6 [2.40]	29.94	34.18	Rubber to Rubber	27
65C	Desmodur VKS-18 [6.30]	Poly bd R45HT [0.72]	From PA-6 [0.90]	Kodaflex DOA [0.48] DOTP from Kodaflex PA-6 [3.60]	28.04	34.90	Rubber to Rubber	30
65D	Desmodur VKS-18 [1.40]	Poly bd R45HT [0.16]	From PA-6 [0.20]	Kodaflex DOA [5.44] DOTP from Kodaflex PA-6 [0.80]	28.30	34.12	Rubber to Rubber	30
65E	Desmodur VKS-18 [0.70]	Poly bd R45HT [0.08]	From PA-6 [0.10]	Kodaflex DOA [2.72] DOTP from Kodaflex PA-6 [0.40]	28.16	34.48	Rubber to Rubber	29
65F	Desmodur VKS-18 [0.99]	Poly bd R45HT [0.12]	From PA-6 [0.15]	Kodaflex DOA [10.14] DOTP from Kodaflex PA-6 [0.80]	27.23	32.54	Rubber to Rubber	30

EXAMPLE 66

Akzo Type 174S (unactivated) (Examples 66A-66F) 1000/I 1.5 TPI and Akzo Type 164S (pre-activated) (Examples 66G-66L) 1000/I 1.5 TPI polyester yarns were treated with each of the solutions of Table 33 by the procedure of Example 19. Each solution in Table 33 contained 20.0% by weight Desmodur VK-18 in addition to the ingredients listed in Table 33. Examples which do not add to 100 percent contained toluene to make up the difference. The treated yarns were tested for adhesion by the procedure of Example 13. The rubber compound was the same carbon filled EPDM as used in Example 15 with the same vulcanization conditions.

TABLE 33

EXAMPLE	FIBER TYPE	HYDROXYL TERM. POLY BUTADIENE ESTER (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lb.)	MAXIMUM LOAD (lb.)	FAILURE TYPE	PULL LENGTH (mm)
66A	Regular (174S)	NONE	NONE	NONE	2.05	3.47	Fiber to Rubber	43
66B	Regular (174S)	Poly bd R45HT [2.0]	NONE	NONE	29.52	38.01	Rubber to Rubber	29
66C	Regular (174S)	NONE	NONE	Kodaflex DOA [80.0]	2.67	3.91	Fiber to Rubber	48
66D	Regular (174S)	Poly bd R45HT [2.0]	NONE	Kodaflex DOA [78.0]	34.80	39.55	Rubber to Rubber	25
66E	Regular (174S)	Poly bd R45HT [2.0]	From PA-6 [3.0]	DOTP from Kodaflex PA-6 [12.0]	33.98	39.43	Rubber to Rubber	25
66F	Regular (174S)	Poly bd R45HT [2.0]	From PA-6 [3.0]	Kodaflex DOA [83.0] DOTP from Kodaflex PA-6 [12.0]	32.57	37.37	Rubber to Rubber	25
66G	Pre-activated (164S)	NONE	NONE	NONE	19.45	25.21	Mixed	34
66H	Pre-activated (164S)	Poly bd R45HT [2.0]	NONE	NONE	35.63	41.13	Rubber to Rubber	25
66I	Pre-activated (164S)	NONE	NONE	Kodaflex DOA [80.0]	18.58	29.08	Mixed	33
66J	Pre-activated (164S)	Poly bd R45HT [2.0]	NONE	Kodaflex DOA [78.0]	37.12	45.51	Rubber to Rubber	25
66K	Pre-activated (164S)	Poly bd R45HT [2.0]	From PA-6 [3.0]	DOTP from Kodaflex PA-6 [12.0]	38.12	46.19	Rubber to Rubber	25
66L	Pre-activated (164S)	Poly bd R45HT [2.0]	From PA-6 [3.0]	Kodaflex DOA [83.0] DOTP from Kodaflex PA-6 [12.0]	34.27	40.17	Rubber to Rubber	25

EXAMPLE 67

A variety of isocyanates and isocyanate derivatives were applied to 1000 denier 1.5 Akzo Type 174S polyester yarn by the procedure of Example 19. Mondur CD in Examples 67A and 67C is a carbodiimide modified diphenylmethane 4,4'-diisocyanate (MDI) from Miles, Inc. Desmodur N-3200 in Example 67D is a hexamethylene diisocyanate based biuret from Miles, Inc. Desmodur N-3300 in Example 67E is the trimer of hexamethylene diisocyanate to form an isocyanurate ring. The Desmodur E-21A in Example 67F is a higher molecular weight polyurethane prepolymer, based on MDI containing reactive isocyanate groups. The treated yarns were tested for adhesion by the procedure of Example 13. The rubber compound was the same carbon filled chlorobutyl rubber as used in Example 37 with the same vulcanization conditions. The results are reported in Table 34 which shows that a variety of isocyanates and isocyanate derivatives can be used in the adhesion system of this invention to provide treated yarn with high adhesion to the chlorobutyl rubber.

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TABLE 34

EXAMPLE	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
67A	Desmodur VKS-18 [8.6] Mondur CD [9.1]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [28.7] Palatinol 711P [28.6] DOTP from Kodaflex PA-6 [20.0]	7.25	8.65	Fiber to Rubber	41
67B	Desmodur VKS-18 [17.2]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [28.9] Palatinol 711P [28.9] DOTP from Kodaflex PA-6 [20.0]	8.38	9.78	Mixed-thin	40
67C	Mondur CD [18.2]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [28.4] Palatinol 711P [28.4] DOTP from Kodaflex PA-6 [20.0]	3.89	4.58	Fiber to Rubber	44
67D	Desmodur N-3200 [23.0]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [24.0] Palatinol 711P [24.0] DOTP from Kodaflex PA-6 [20.0]	5.09	5.97	Fiber to Rubber	42
67E	Desmodur N-3300 [24.8]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [23.1] Palatinol 711P [23.1] DOTP from Kodaflex PA-6 [20.0]	6.73	7.68	Fiber to Rubber	40
67F	Desmodur E-21 [33.3]	Poly bd R45HT [4.0]	From PA-6 [5.0]	Kodaflex DOA [18.9] Palatinol 711P [18.9] DOTP from Kodaflex PA-6 [20.0]	5.45	6.65	Fiber to Rubber	41

EXAMPLE 68

The poly maleate ester used in the previous examples was studied more extensively by comparing the commercial mixture (Kodaflex PA-6 from Eastman Chemical Company) (Examples 68A and 68D), which is
5 approximately 80/20 by weight of a mixture of bis(2-ethylhexyl)-terephthalate (CAS# 6422-86-2) to poly(2,2,4-trimethyl-1,3-pentanediol maleate) (CAS# 25085-65-8), with a laboratory prepared mixture of approximately 80/20 by weight of a mixture of bis(2-ethylhexyl)-terephthalate as Kodaflex DOTP from Eastman Chemical Company with
10 poly(2,2,4-trimethyl-1,3-pentanediol maleate) prepared in the laboratory by the procedure of Example 1 of U.S. Patent 3,466,264 issued to Eastman Kodak Company (Hagemeyer, Jr. et al.) on September 9, 1969 (Examples 68B and 68E). Also, Example 68C in Table 35 uses a laboratory prepared mixture of approximately 80/20 by weight of a mixture of bis(2-ethylhexyl)
15 adipate as Kodaflex DOA from Eastman Chemical Company with the same poly(2,2,4-trimethyl-1,3-pentanediol maleate) prepared in the laboratory. In Example 68C, the 20 parts of the lab made poly(2,2,4-trimethyl-1,3-pentanediol maleate) was dissolved in 80 parts Kodaflex DOA. This solution (12.5 parts) was then added to the mixture of Poly bd R45HT and
20 43.3 parts of the Kodaflex DOA listed in Example 68C of Table 35. The various formulations in Table 35 were applied to 1000 denier 1.5 Akzo Type 174S polyester yarn by the procedure of Example 55. The treated yarns were tested for adhesion by the procedure of Example 13. The rubber compound in Table 35 was a different carbon filled chlorinated
25 sulfonated polyethylene (Hypalon) than was used in Example 57. This rubber compound was milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 325°F for 30 minutes at 3200 PSI. The results are reported in Table 35.

TABLE 35

EXAMPLE	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lb.)	MAXIMUM LOAD (lb.)	FAILURE TYPE	PULL LENGTH (mm)
68A	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	Poly 2,2,4-Trimethyl- 1,3-Pentene Diol Maleate from Kodaflex PA-6 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	13.84	18.12	Mixed-thin	28
68B	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	Poly 2,2,4-Trimethyl- 1,3-Pentene Diol Maleate Made in Lab By Example One U.S. 3,466,264 [2.5]	Kodaflex DOA [43.3] Palatinol 711P [25.0] DOTP [10.0]	13.35	20.98	Rubber Broke	15
68C	Desmodur VKS-18 [17.2]	Poly bd R45HT [2.0]	As Example 68B	Kodaflex DOA [53.3] Palatinol 711P [25.0]	10.83	20.51	Rubber Broke	8
68D	Desmodur VKS-18 [17.2]	None	As Example 68A	Kodaflex DOA [45.3] Palatinol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	13.75	20.75	Rubber Broke	8
68E	Desmodur VKS-18 [17.2]	None	As Example 68B	Kodaflex DOA [45.3] Palatinol 711P [25.0] DOTP [10.0]	11.49	23.22	Rubber Broke	7
68F	Desmodur VKS-18 [17.2]	None	None	Kodaflex DOA [47.8] Palatinol 711P [25.0] DOTP from Eastman Chemical Company [10.0]	2.37	3.09	Fiber to Rubber	44

EXAMPLE 69

5 Example 69 expands on Examples 50 and 51 by showing the effect of different terminal groups of butadiene polymers combined with the polymaleate ester component. The polyester used, method of application and method of testing was the same as in Examples 50 and 51. A mineral filled EPDM rubber compound, milled to a thickness of 0.100 to 0.120 inches, used to make commercial hoses was used in the adhesion testing. The vulcanization conditions were 325°F for 30 minutes. The results are shown in Table 36.

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TABLE 36

EXAMPLE	ISOCYANATE (% BY WEIGHT)	BUTADIENE POLYMER END GROUP TYPE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lb _f)	MAXIMUM LOAD (lb _f)	FAILURE TYPE	PULL LENGTH (mm)
69A	Desmodur VKS-18 [17.2]	Hydroxyl (Poly bd R45HT) [2.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatrol 711P [25.0] DOTP from Kodaflex PA-6 [10.0]	15.03	18.08	Rubber to rubber	30
69B	Desmodur VKS-18 [17.2]	Acrylate (Poly bd 300) [2.0]	From PA-6 [2.5]	As Example 69A	17.74	20.09	Rubber to Rubber	30
69C	Desmodur VKS-18 [17.2]	Hydroxyl & Epoxy (Poly bd 605) [2.0]	From PA-6 [2.5]	As Example 69A	18.15	20.99	Rubber to Rubber	27
69D	Desmodur VKS-18 [17.2]	Hydroxyl & Epoxy (Poly bd 600) [2.0]	From PA-6 [2.5]	As Example 69A	18.34	21.05	Rubber to Rubber	25
69E	Desmodur VKS-18 [17.2]	Carboxylic Acid (SPP 525) [2.0]	From PA-6 [2.5]	As Example 69A	17.41	20.53	Rubber to Rubber	27
69F	Desmodur VKS-18 [17.2]	Phenyl (SPP 443) [2.0]	From PA-6 [2.5]	As Example 69A	15.33	19.01	Rubber to Rubber	28
69G	Desmodur VKS-18 [17.2]	Acrylate-Acrylonitrile Copolymer (SPP 516) [2.0]	From PA-6 [2.5]	As Example 69A	14.25	16.83	Rubber to Rubber	31
69H	Desmodur VKS-18 [17.2]	Acrylate-Acrylonitrile Copolymer (SPP 522) [2.0]	From PA-6 [2.5]	As Example 69A	17.54	20.06	Rubber to Rubber	28
69I	Desmodur VKS-18 [17.2]	Amine-Acrylonitrile Copolymer (SPP 517) [2.0]	From PA-6 [2.5]	As Example 69A	17.71	20.85	Rubber to Rubber	28
69J	Desmodur VKS-18 [17.2]	As 69F [12.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatrol 711P [15.0] DOTP from Kodaflex PA-6 [10.0]	18.29	21.98	Rubber to Rubber	23
69K	Desmodur VKS-18 [17.2]	As 69E [12.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatrol 711P [15.0] DOTP from Kodaflex PA-6 [10.0]	20.06	25.00	Rubber to Rubber	21
69L	Desmodur VKS-18 [17.2]	As 69B [12.0]	From PA-6 [2.5]	Kodaflex DOA [43.3] Palatrol 711P [15.0] DOTP from Kodaflex PA-6 [10.0]	19.48	23.88	Rubber to Rubber	24

EXAMPLE 70

5 Table 37 demonstrates a significant advantage of this invention in regard to energy requirements. No heat treatment is required to impart the adhesion improvements at various molar ratios of isocyanate to hydrocarbon polymer. This table further demonstrates the uniqueness of the invention in regard to the molar ratio of isocyanate to hydrocarbon polymer requirements and the advantage of the addition of a plasticizer.

10 All solutions were applied to 1000/I 1.5TPI polymers Type 174S from Akzo fibers as in Example 1 except for heat treatment as noted in Table 37. The treated fibers were tested for adhesion as in Example 13 using the same carbon filled EPDM rubber as in Example 14 milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were the same as in Example 14.

TABLE 37

EXAMPLE	POLYMETHYLENE POLYPHENYL ISOCYANATE (WT. %)	OH TERM. POLY BUTADIENE (WT. %)	TOLUENE (WT. %)	DIOCTYL ADIPATE (WT. %)	HEAT TREATMENT AFTER CHEMICALS APPLIED	MEAN LOAD (lb.)	MAXIMUM LOAD (lb.)	FAILURE TYPE	PULL LENGTH (mm)
70A	17.2	0	82.8	0	220 MINUTES AT 200°F	3.13	4.07	Fiber to Rubber	43
70B	17.2	0	82.8	0	NONE	3.01	4.23	Fiber to Rubber	43
70C	17.2	0	0	82.8	220 MINUTES AT 200°F	11.18	13.39	Rubber to Rubber	36
70D	17.2	0	0	82.8	NONE	11.44	12.80	Rubber to Rubber	34
70E	17.2	3.2	79.6	0	220 MINUTES AT 200°F	11.47	14.49	Rubber to Rubber	30
70F	17.2	3.2	79.6	0	NONE	7.47	8.43	Mixed	40
70G	17.2	3.2	0	79.6	220 MINUTES AT 200°F	11.58	13.46	Rubber to Rubber	31
70H	17.2	3.2	0	79.6	NONE	11.71	13.14	Rubber to Rubber	34
70I	17.2	15.8	67.0	0	220 MINUTES AT 200°F	11.67	13.88	Mixed	35
70J	17.2	15.8	67.0	0	NONE	8.96	10.76	Mixed	38
70K	17.2	15.8	0	67.0	220 MINUTES AT 200°F	12.48	13.82	Rubber to Rubber	34
70L	17.2	15.8	0	67.0	NONE	11.70	13.02	Rubber to Rubber	35
70M	17.2	63.2	19.6	0	220 MINUTES AT 200°F	7.70	8.13	Mixed	40
70N	17.2	63.2	19.6	0	NONE	3.30	4.67	Fiber to Rubber	44
70O	17.2	63.2	0	19.6	220 MINUTES AT 200°F	6.92	8.85	Mixed	41
70P	17.2	63.2	0	19.6	NONE	3.74	5.25	Fiber to Rubber	44
70Q	3.7	13.5	82.8	0	220 MINUTES AT 200°	8.93	12.41	Mixed	40
70R	3.7	13.5	82.8	0	NONE	4.72	5.88	Mixed	42
70S	3.7	13.5	0	82.8	220 MINUTES AT 200°F	11.85	13.15	Rubber to Rubber	35
70T	3.7	13.5	0	82.8	NONE	10.82	13.47	Mixed	35

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EXAMPLES 71, 72 AND 73

Other polyunsaturated polyesters were made in the lab as in Example 68 by substituting 1,6-hexanediol for 2,2,4-trimethyl-1,3-pentanediol (Examples 74E and 74F) and by substituting itaconic anhydride for maleic anhydride (Examples 71D and 72D). Examples 71C and 72C have a change in the molar ratio of the maleic anhydride and 2,2,4-trimethyl-1,3-pentanediol. All solutions were made by the procedure of Example 68 and applied to 1000/1 1.5 TPI Akzo Type 174S polyester yarn as in Example 68 and tested for adhesion as in Example 13. Examples 71 and 73 used the same carbon filled Hypalon compound and vulcanization conditions as in Example 57. Example 72 used the same carbon filled EPDM compound and vulcanization conditions as in Example 15. The results for Examples 71, 72 and 73 are shown in Tables 38, 39 and 40, respectively.

EXAMPLE 74

Table 41 shows the effect of different types of polymers and terminal groups on adhesion with a Hypalon (chlorinated sulfonated polyethylene) compound. The effect of the polymaleate ester with the isocyanate and plasticizer on this compound should be noted. All treatments were applied to the same yarn and by the same procedure as in Example 19. The adhesion was tested as in Example 13. The same carbon filled Hypalon compound and vulcanization conditions from Example 68 was used.

In Table 41, the molar ratios of isocyanate to polymer terminal group were calculated as in Example 50. In the case of polymaleate ester, an acid number of 3.16 meqKOH/g for Kodaflex PA-6 was used to calculate an equivalent weight (EW) using the following formula:

$$EW = 56,100/\text{Acid Number.}$$

EXAMPLE 75

The versatility of this adhesion system was examined by applying the solutions in Examples 75A, 75B, 75C and 75D each to a 0.005 inch thick 6" x 6" sheet of polyester film. A clean 6" x 6" preweighed sheet, taped on one side using the masking tape from Example 13, was evenly coated, on the untaped side, with each example solution by means of a soft bristle brush. The samples were weighed immediately after coating, and a pick-up was determined using the formula: $100 \times (\text{wet weight} - \text{dry weight}) / (\text{dry weight})$. Each coated sheet was placed in an oven at 93°C for 220 minutes and removed and allowed to cool at ambient temperatures before adhesion testing. Four 1" x 3 15/16" sections of aluminum foil were cut to allow the film to be separated from the rubber when testing using the general procedure in Example 13 with the noted exceptions. A 3 15/16" x 3 15/16" section was cut from each 6" x 6" sheet and tested using the mold from Example 49. The same EPDM compound from Example 14 was used except milled to a thickness of 0.100 to 0.120 inches. The vulcanization conditions were 325°F for 30 minutes at 3200 psi. The results are shown in Table 42.

EXAMPLE 76

Table 43 summarizes the invention by comparing two commercial adhesive treated polyester yarns (RFL and Non-RFL) used for hose reinforcement (both on Akzo Type 174S 1500 Denier 1.5 TPI polyester) with a preferred embodiment of this invention in respect to adhesion, yarn processing and solution stability (also on 1500 denier 1.5 TPI Akzo Type 174S polyester yarn). All three yarns had been wound on cones for processing into hoses. The same carbon filled EPDM compound and vulcanization conditions from Example 15 was used in Example 76. This preferred embodiment of this invention was applied to yarn as in Example 58.

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The results in Table 43 show significantly improved adhesion is obtained from yarn treated with the preferred adhesion system over commercial yarns.

TABLE 38

EXAMPLE	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
71A	Desmodur VKS-18 [17.2]	None	Poly 2,2,4-Trimethyl- 1,3-Pentene Diol Maleate from Kodaflex PA-6 [5.0]	Kodaflex DOA [42.8] Palatinol 711P [15.0] DOTP from Kodaflex PA-6 [20.0]	9.41	10.79	Rubber to Rubber	41
71B	Desmodur VKS-18 [17.2]	None	Poly 2,2,4-Trimethyl- 1,3-Pentene Diol Maleate Made In Lab By Example One U.S. 3,466,264 [5.0]	Kodaflex DOA [42.8] Palatinol 711P [15.0] Kodaflex DOTP	8.98	10.70	Rubber to Rubber	40
71C	Desmodur VKS-18 [17.2]	None	As Example 71B but 1.0/1.1 Molar Ratio Diol to Maleic Anhydride [5.0]	Kodaflex DOA [42.8] Palatinol 711P [15.0] Kodaflex DOTP [20.0]	9.01	10.88	Rubber to Rubber	40
71D	Desmodur VKS-18 [17.2]	None	As Example 71B but Itaconic Anhydride Replaced Maleic Anhydride [5.0]	Kodaflex DOA [42.8] Palatinol 711P [15.0] Kodaflex DOTP [20.0]	8.03	9.72	Mixed	41
71E	Desmodur VKS-18 [17.2]	None	None	Kodaflex DOA [42.8] Palatinol 711P [15.0] Kodaflex DOTP [25.0]	1.97	2.92	Fiber to Rubber	43

TABLE 39

EXAMPLE	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE, ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lb.f.)	MAXIMUM LOAD (lb.f.)	FAILURE TYPE	PULL LENGTH (mm)
72A	Desmodur VKS-18 [17.2]	None	Poly 2,2,4-Trimethyl- 1,3-Pentene Diol Maleate from Kodaflex PA-6 [5.0]	Kodaflex DOA [42.8] Palatinol 711P [15.0] DOTP from Kodaflex PA-6 [20.0]	11.28	14.08	Mixed	40
72B	Desmodur VKS-18 [17.2]	None	Poly 2,2,4-Trimethyl- 1,3-Pentene Diol Maleate Made in Lab By Example One U.S. 3,466,264 [5.0]	Kodaflex DOA [42.8] Palatinol 711P [15.0] Kodaflex DOTP	9.31	12.44	Mixed	40
72C	Desmodur VKS-18 [17.2]	None	As Example 72B but 1.0/1.1 Molar Ratio Diol to Maleic Anhydride [5.0]	Kodaflex DOA [42.8] Palatinol 711P [15.0] Kodaflex DOTP [20.0]	3.00	4.47	Fiber to Rubber	44
72D	Desmodur VKS-18 [17.2]	None	As Example 72B but Iteconic Anhydride Replaced Maleic Anhydride [5.0]	Kodaflex DOA [42.8] Palatinol 711P [15.0] Kodaflex DOTP [20.0]	1.21	2.60	Fiber to Rubber	45
72E	Desmodur VKS-18 [17.2]	None	None	Kodaflex DOA [42.8] Palatinol 711P [15.0] Kodaflex DOTP [25.0]	2.09	3.14	Fiber to Rubber	48

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TABLE 40

EXAMPLE	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (% BY WEIGHT)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
73A	Desmodur VKS-18 [17.2]	None	None	Kodaflex DOA [42.8] Pelatinal 711P [15.0] DOTP [25.0]	2.12	3.15	Fiber to Rubber	45
73B	Desmodur VKS-18 [17.2]	None	Poly 2,2,4-Trimethyl- 1,3-Pentene Diol Maleate Made In Lab By Example One U.S. 3,486,264 [5.0]	Kodaflex DOA [42.8] Pelatinal 711P [15.0] Kodaflex DOTP	8.27	10.11	Mixed-Thin	41
73C	Desmodur VKS-18 [17.5]	None	As Example 73B	Toluene [77.5]	5.86	7.55	Mixed-Thin	42
73D	Desmodur VKS-18 [17.5]	Poly bd R45HT [2.0]	As Example 73B	Toluene [75.5]	6.15	7.62	Mixed-Thin	42
73E	Desmodur VKS-18 [17.5]	Poly bd R45HT [2.0]	As Example 73B but 1,6-Hexanediol Replaced 2,2,4- Trimethyl-1,3-Pentene Diol	Toluene [75.5]	5.43	6.96	Mixed	43
73F	Desmodur VKS-18 [17.5]	None	As Example 73E	Toluene [77.5]	3.82	4.95	Mixed	43

TABLE 41*

EXAMPLE	POLYMETHYLENE POLYIMIDYL ISOCYANATE (wt. %)	TYPE OF POLYUNSATU- RATED POLYMER	WT. % POLYUNSATU- RATED POLYMER	POLYMER END GROUPS	MOLAR RATIO ISOCYANATE TO POLYMER TERMINAL GROUPS	DIOCTYL TEREPHTHALATE (WT. %)	MEAN LOAD (lbs.)	MAXIMUM LOAD (lbs.)	FAILURE TYPE	PULL LENGTH (mm)
74A	17.5	NONE	NONE	NONE	N/A	82.80	4.04	4.75	Fiber to Rubber	41
74B	17.5	BUTADIENE	3.35	Hydroxyl	48 to 1	79.20	7.39	9.04	Fiber to Rubber	38
74C	17.5	BUTADIENE	3.28	Carbonyl	98 to 1	79.24	4.72	5.94	Fiber to Rubber	41
74D	17.5	BUTADIENE	3.39	Phenyl	88 to 1	79.11	4.06	6.37	Fiber to Rubber	41
74E	17.5	BUTADIENE	3.50	Acrylate	82 to 1	78.94	6.50	7.67	Mixed-thin	39
74F	17.5	POLY MALEATE FROM KODAFLEX PA-6	4.87	Carbonyl	102 to 1	89.06 from Kodaflex DOTP 19.27 from Kodaflex PA-6	14.48	23.00	Rubber broke	12
74G	4.58	BUTADIENE	16.17	Hydroxyl	2.56 to 1	79.25	3.96	5.25	Fiber to Rubber	41
74H	4.57	BUTADIENE	16.19	Carbonyl	5.03 to 1	79.24	0.77	1.53	Fiber to Rubber	39
74I	4.46	BUTADIENE	16.43	Phenyl	3.47 to 1	79.11	1.37	2.04	Fiber to Rubber	42
74J	4.32	BUTADIENE	16.74	Acrylate	2.72 to 1	78.94	0.85	1.72	Fiber to Rubber	38
74K	1.55	POLY MALEATE FROM KODAFLEX PA-6	16.21	Carbonyl	2.55 to 1	17.41 from Kodaflex DOTP 64.83 from Kodaflex PA-6	4.18	5.56	Fiber to Rubber	41
74L	17.5	NONE	None	N/A	1 to 0	82.50	2.84	4.20	Fiber to Rubber	41

*wt. % values, in Table 41, are given to an accuracy of ± 0.02 .

TABLE 42

EXAMPLE	POLYMETHYLENE POLYPHENYL ISOCYANATE (WT.%)	HYDROXYL TERM. POLY BUTADIENE (WT.%)	TOLUENE (WT.%)	DIOCTYL ADIPATE (WT.%)	% PICK-UP	MEAN LOAD (lb.)	MAXIMUM LOAD (lb.)	FAILURE TYPE	PULL LENGTH (mm)
75A	20.0	0.0	80.0	0.0	11.7	1.32	2.44	Film to Rubber	38
75B	20.0	0.0	0.0	80.0	11.4	0.93	2.30	Film to Rubber	43
75C	20.0	5.0	75.0	0.0	12.2	1.85	4.84	Mixed with more Film to Rubber than Rubber to Rubber	38
75D	20.0	5.0	0.0	75.0	12.3	6.79*	13.32	Rubber Broke	19

*NOTE: The mean load is lower due to the fact that the rubber broke with very little extension of the tester.

TABLE 43

EXAMPLE	ISOCYANATE (% BY WEIGHT)	HYDROXYL TERM. POLY BUTADIENE (WT. %)	POLY MALEATE ESTER (% BY WEIGHT)	PLASTICIZER (% BY WEIGHT)	MEAN LOAD (lbf.)	MAXIMUM LOAD (lbf.)	FAILURE TYPE	PULL LENGTH (mm)
76A	COMMERCIAL	RFL	TREATED	YARN	6.32	8.52	Fiber to Rubber	41
76B	COMMERCIAL	NON-RFL	TREATED	YARN	5.29	7.01	Fiber to Rubber	42
76C	Desmodur VKS-18 (17.2)	2.0	From PA-6 (2.5)	Kodaflex DOA (43.3) Palatinal 711P (25.0) DOTP from Kodaflex PA-6 (10.0)	24.48	29.52	Rubber to Rubber	30

•NOTE: The mean load is lower due to the fact that the rubber broke with very little extension of the tester.

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The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

- 5 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

WHAT IS CLAIMED IS:

1. An adhesion system which comprises:

a) an isocyanate compound containing two or more isocyanate groups;

b) i) one or more of a hydrocarbon polymer having more than one carbon-to-carbon double bond unit formed from polyenes and dienes and having one or more of a hydroxyl, thiol, amine or carboxyl functional group or a combination thereof, per polymer molecule, and/or a reaction product of such a hydrocarbon polymer with an isocyanate compound of a), wherein the molar ratio of isocyanate groups of a) to hydroxyl, thiol, amine and carboxylic acid functional groups is equal to or greater than 2.5 to 1; or

ii) one or more of a heteroatom polymer having more than one carbon-to-carbon double bond unit, or other group capable of forming a carbon-to-carbon double bond, per polymer molecule, or otherwise capable of undergoing free radical reaction, formed by reaction of one or more saturated or unsaturated carboxylic acids or acid derivatives with one or more saturated or unsaturated polyols, polythiols or polyamines or compounds with a mixture of such functional groups, and having one or more of a hydroxyl, thiol, amine or carboxylic acid function group and/or a reaction product of such a heteroatom polymer with an isocyanate compound of a); or

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iii) one or more of a hydrocarbon polymer of b)i) and one or more of a heteroatom polymer of b)ii),

c) one or more of a liquid plasticizer,
wherein a) and b)i) and b)ii) and b)iii) are soluble or dispersible in said liquid plasticizer.

2. An adhesion system which is suitable for aiding adhesion of reinforcement material, which comprises

a) one or more of an isocyanate compound selected from the group consisting of polymethylene polyphenyl isocyanate, toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), meta-tetramethylxylene diisocyanate, bis(4-isocyanatocyclohexyl)methane, (1,4-bisisocyanatomethyl) cyclohexane, isophorone diisocyanate (IPDI), diphenylmethane 4,4'-diisocyanate (MDI), p-xylene diisocyanate, toluene triisocyanate, the biuret of hexamethylene diisocyanate, the adduct of TDI with trimethylol propane, the trimers (isocyanurate ring) of TDI and HDI, copolymers of TDI and HDI; the dimer of TDI; the caprolactam, phenol, substituted phenol, or butanone oxime blocked TDI and HDI, polycarbodiimide modified MDI and polyureas of TDI, 1,4-benzene diisocyanate, dianisidine diisocyanate, 1-chlorophenyl-2,4-diisocyanate, trimethylene diisocyanate, pentamethylene diisocyanate, butylene-1,2-diisocyanate, butylene-1,4-diisocyanate, xylene diisocyanate, 2,4-cyclohexanediiisocyanate, 1,4-cyclohexanediiisocyanate, 1,1-dibutylether diisocyanate, 1,6-cyclopentane diisocyanate, 2,5-indene diisocyanate, 1,5-naphthalene diisocyanate, triphenylmethane diisocyanate, 1,12-diisocyanatododecane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane and 4,4'-diisocyanatodicyclohexylpropane-(2,2),

b) i) one or more of a hydrocarbon polymer having more than one carbon-to-carbon double bond unit, per polymer molecule,

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derived from a diene monomer selected from the group consisting of butadiene, isoprene, chloroprene and 2,3-dimethylbutadiene, 2,4-hexadiene, ethylidene norbornene, 1,4-hexadiene, dicyclopentadiene and cyclopentene and optionally comonomers selected from the group consisting of isobutylene, ethylene, propylene, butene, vinyl ethers, styrene, vinyl toluene, vinyl pyridine, acrylonitrile and acrylic and methacrylic acids, amides and esters, having more than one hydroxyl or carboxyl, thiol or amine functional group and/or a reaction product of such hydrocarbon polymer with a), wherein the molar ratio of isocyanate groups of a) to hydroxyl, thiol, amine or carboxyl functional groups is equal to or greater than 2.5:1; or

ii) one or more of a polyester having more than one carbon-to-carbon double bond unit per polymer molecule derived from monomers selected from:

unsaturated dicarboxylic acids selected from the group consisting of maleic, itaconic, citraconic, fumaric, trans-3-hexene-dioic acids, 1-cyclopentene-1,2-dicarboxylic anhydride, and alkenyl substituted succinic anhydrides;

saturated dicarboxylic acids selected from the group consisting of succinic, phthalic, terephthalic and trimellitic acids,

saturated diols selected from the group consisting of 2,2,4-trimethyl-1,3-pentanediol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, 2,4-dimethyl-2-ethyl-1,3-hexanediol, 1,6-hexanediol, 1,5-hexanediol, 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 7-octene-1,2-diol, 5-norbornene-2,2-dimethanol, ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol, 2,2'-thiodiethanol, 1,3-propanediol, 2-methyl-1,3-propanediol, resorcinol, 1,3-dihydroxynaphthalene, cyclohexane dimethanol, 2-amino-2-ethyl-1,3-propanediol, 2,4-dihydroxybenzoic acid,

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and

unsaturated polyols selected from the group consisting of 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 2-octene-1,2-diol, dihydroxy fumaric acid, 5-norbornene-2,2-dimethanol, 3-allyloxy-1,2-propanediol, cis-3,5-cyclohexadiene-1,2-diol, 2,3-dihydroxypropylacrylate and methacrylate, N,N'-(1,2-dihydroxyethylene)bisacrylamide, dihydroxycinnamic acid; and

having hydroxyl, carboxyl, thiol or amine functional groups or a combination thereof; and/or a reaction product of such polyester with a), or

iii) one or more of a hydrocarbon polymer of b)i) and one or more of a polyester of b)ii);

c) one or more of a plasticizer which is liquid at ambient temperature selected from the group consisting of organic esters; inorganic esters; amides; hydrocarbons; halogenated derivatives of organic esters, inorganic esters and hydrocarbons; epoxidized derivatives of organic esters, inorganic esters and hydrocarbons; silanes and mixtures thereof; wherein a), b)i), b)ii) are soluble or dispersible in said liquid plasticizer of c).

3. An adhesion system which is suitable for aiding adhesion of reinforcement material, which comprises

a) polymethylene polyphenyl isocyanate,

b) i) one or more of a hydrocarbon homopolymer or copolymer of 1,3-butadiene, isoprene, chloroprene and 2,3-dimethylbutadiene containing more than one carbon-to-carbon double bond unit per polymer molecule and having one or more of a hydroxyl, carboxyl, thiol or amine functional group and/or a reactive product of such hydrocarbon polymer with a), wherein the molar ratio of isocyanate groups of a) to hydroxyl,

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thiol, amine or carboxyl functional groups is equal to or greater than 2.5:1; or

ii) one or more of a polyester having more than one carbon-to-carbon double bond unit per polymer molecule formed by the reaction of maleic, itaconic, or citraconic acid, anhydride or other derivatives with 2,2,4-trimethyl-1,3-pentadiol or 2-methyl-1,3-propane diol, and having hydroxyl and/or carboxyl functional groups; and/or a reaction product of such polyester with a), or

iii) one or more of a hydrocarbon polymer of b)i) and one or more of a polyester of b)ii);

c) one or more of a plasticizer which is liquid at ambient temperature selected from the group consisting of (bis-2-ethylhexyl)-terephthalate, dioctyladipate, dibutylphthalate, C₈-C₁₁-dialkylphthalate, 2,2,4-trimethyl-3-pentyl-diisobutyrate, di(2-ethylhexyl)adipate, di(2-ethylhexyl)phthalate, di(2-ethylhexyl)terephthalate, di(n-octyl)adipate, di(n-octyl)phthalate, di(n-octyl)terephthalate, di(isooctyl)adipate, di(isooctyl)phthalate, di(isooctyl)terephthalate, di(C₇-C₁₁-alkyl)adipate, di(C₇-C₁₁-alkyl)phthalate, di(C₇-C₁₁-alkyl)terephthalate, diisobutyl adipate, mixed C₄-C₁₁-alkylphthalates, diundecyl phthalate, dinonyl adipate, di(n-decyl adipate), (n-decyl, n-octyl) adipate and (2-ethylhexyl, n-octyl) adipate;

wherein a), b)i), b)ii) are soluble and dispersible in said liquid plasticizer of c).

4. An adhesion system as in claim 2, wherein the hydrocarbon polymer has an average of at least three unsaturated carbon-to-carbon double bond units or other groups capable of forming carbon-to-carbon double bonds per polymer molecule and the heteroatom polymer has an average of at least three unsaturated carbon-to-carbon double bond units

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or other groups capable of forming carbon-to-carbon double bonds per polymer molecule.

5. An adhesion system as in claim 1, wherein the hydrocarbon polymer has an average of at least five and the heteroatom polymer has an average of at least eight unsaturated carbon-to-carbon double bond units or other groups capable of forming carbon-to-carbon double bonds per polymer molecule.

6. An adhesion system as in claim 2, wherein the hydrocarbon polymer has an average of at least ten unsaturated carbon-to-carbon double bond units per polymer molecule and the polyester has an average of from 3-20 unsaturated carbon-to-carbon double bond units per polymer molecule.

7. An adhesion system as in claim 2, wherein the hydrocarbon homopolymer is a polybutadiene homopolymer.

8. An adhesion system as in claim 1, wherein a portion of the hydroxyl, carboxyl, thiol or amine terminal functional groups on the hydrocarbon polymer are replaced with non-reactive groups.

9. An adhesion system as in claim 1, wherein a portion of the carbon-carbon double bonds in the hydrocarbon polymer are replaced by epoxy groups.

10. An adhesion system as in claim 1, wherein the hydrocarbon polymer is a polybutadiene homopolymer or copolymer with non-reactive terminal groups.

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11. An adhesion system as in claim 1, wherein the hydrocarbon polymer has an average of 0.1 to 50 reactive functional groups per polymer molecule.

12. An adhesion system as in claim 1, wherein the molar ratio of isocyanate and isocyanate equivalent groups to reactive functional groups on the hydrocarbon polymer and/or heteroatom polymer is equal to or greater than 5:1.

13. An adhesion system as in claim 1, wherein the molar ratio of isocyanate and isocyanate equivalent groups to reactive functional groups on the hydrocarbon polymer and/or heteroatom polymer is equal to or greater than 25:1.

14. An adhesion system as in claim 2, wherein the molar ratio of isocyanate and isocyanate equivalent groups to reactive functional groups on the hydrocarbon polymer and/or heteroatom polymer is greater than 100:1.

15. An adhesion system as in claim 1, wherein the heteroatom polymer is

i) one or more of a polyester derived from monomers selected from:

unsaturated dicarboxylic acids selected from the group consisting of maleic, itaconic, citraconic, fumaric, trans-3-hexene-dioic acids and 1-cyclopentene-1,2-dicarboxylic anhydride, and alkenyl substituted succinic anhydrides;

saturated dicarboxylic acids selected from the group consisting of succinic, phthalic, terephthalic and trimellitic acids,

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saturated diols selected from the group consisting of 2,2,4-trimethyl-1,3-pentanediol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, 2,4-dimethyl-2-ethyl-1,3-hexanediol, 1,6-hexanediol, 1,5-hexanediol, 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 7-octene-1,2-diol, 5-norbornene-2,2-dimethanol, ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol, 2,2'-thiodiethanol, 1,3-propanediol, 2-methyl-1,3-propanediol, resorcinol, 1,3-dihydroxynaphthalene, cyclohexane dimethanol, 2-amino-2-ethyl-1,3-propanediol, 2,3-dihydroxypropylacrylate and methacrylate, dihydroxycinnamic acid, 2,4-dihydroxybenzoic acid; and

unsaturated polyols selected from the group consisting of 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 2-octene-1,2-diol, 3-allyloxy-1,2-propanediol, 5-norbornene-2,2-dimethanol, N,N'-(1,2-dihydroxyethylene)bisacrylamide, cis-3,5-cyclohexadiene-1,2-diol; dihydroxyfumaric acid and having hydroxyl, carboxyl, thiol or amine functional groups or a mixture thereof; and/or a reaction product of such polyunsaturated polyester with a),

ii) one or more of a polyamide derived from saturated polyamines selected from the group consisting of 1,6-diaminehexane, 1,2-diamino-2-methylpropane or mixtures thereof and unsaturated dicarboxylic acids as in i)

iii) one or more of a polythiol derived from saturated dithiols selected from the group consisting of 1,6-hexane dithiol, 2,2'-dithiol diethanol, dithiolaerythritol, 1,4-butanedithiol, 2,3-butanedithiol and unsaturated dicarboxylic acids as in i); or

iv) a mixture thereof.

16. An adhesion system as in claim 1, wherein the heteroatom polymer is a polyester derived from maleic anhydride or itaconic anhydride

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and a polyol selected from the group consisting of 2,2,4-trimethylpentane-1,3-diol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, 2,4-dimethyl-2-ethyl-1,3-hexanediol, 1,6-hexanediol, 1,5-hexanediol, 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol, 1,3-propanediol, cyclohexane dimethanol, 3-allyloxy-1,2-propanediol, 2-amino-2-ethyl-1,3-propanediol, glycerol, trimethylol propane, pentaerythritol, unsaturated polyols selected from the group consisting of 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 2-octene-1,2-diol, 5-norbornene-2,2-dimethanol, cis-3,5-cyclohexadiene-1,2-diol and combinations thereof.

17. An adhesion system as in claim 2, wherein the polyester is derived from maleic anhydride, itaconic or citraconic anhydride and a polyol.

18. An adhesion system as in claim 1, wherein the plasticizer is selected from dioctylterephthalate, di(2-ethylhexyl)adipate, di(2-ethylhexyl)phthalate, di(2-ethylhexyl)terephthalate, di(n-octyl)adipate, di(n-octyl)phthalate, di(n-octyl)terephthalate, di(isooctyl)adipate, di(isooctyl)phthalate, di(isooctyl)terephthalate, di(C₇-C₁₁-alkyl)adipate, di(C₇-C₁₁-alkyl)phthalate, di(C₇-C₁₁-alkyl)terephthalate, diisobutyl adipate, mixed C₄-C₁₁-alkylphthalates, diundecyl phthalate, dinonyl adipate, di(n-decyl adipate), (n-decyl, n-octyl) adipate and (2-ethylhexyl, n-octyl) adipate; (bis-2-ethylhexyl)-terephthalate, dioctyladipate, dibutylphthalate, C₈-C₁₁-dialkylphthalate, 2,2,4-trimethyl-3-pentyl-diisobutyrate and mixtures thereof.

19. An adhesion system as in claim 1, wherein the carrier is a

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plasticizer selected from branched and straight chain C₁-C₂₂ alkyl, C₆-C₂₀ aromatic and C₇-C₂₂ alkyl aromatic adipates, phthalates, terephthalates, glutamates, azeolates, sebacates, dodecanates and phosphates.

20. An adhesion system as in claim 3 in the form of a treating solution which consists of from 1 to 75 wt.% polymethylene polyphenyl isocyanate, from 0.5 to 50 wt.% of the polyunsaturated polymer and from 10 to 90 wt.% plasticizer.

21. An adhesion system as in claim 20 in the form of two or more parts.

22. An adhesion system which comprises:

a) an isocyanate compound;

b) i) a hydrocarbon polymer having more than one carbon-to-carbon double bond unit per polymer molecule and having functional groups capable of reacting with an isocyanate compound of a), and/or a reaction product of such a hydrocarbon polymer with an isocyanate compound of a) wherein the molar ratio of isocyanate and isocyanate equivalent groups of a) to reactive functional groups is equal to or greater than 5.0 to 1; or

ii) a heteroatom polymer having more than one carbon-to-carbon double bond unit, per polymer molecule, and having functional groups capable of reacting with an isocyanate compound of a) and/or a reaction product of such a heteroatom polymer with an isocyanate compound of a); or

iii) a hydrocarbon polymer of b)i) and a heteroatom polymer of b)ii); and

c) one or more of a liquid carrier;

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wherein a) and b)i) and b)ii) and b)iii) are soluble or dispersible in said liquid carrier.

23. An article of manufacture for bonding to rubber, elastomeric articles and other unsaturated polymers which comprises a reinforcement material and an adhesion system deposited thereon, said adhesion system resulting from admixture of:

a) an isocyanate compound containing two or more isocyanate groups;

b) i) one or more of a hydrocarbon polymer having more than one carbon-to-carbon double bond unit formed from polyenes and dienes and having one or more of a hydroxyl, thiol, amine or carboxyl functional group or a combination thereof, per polymer molecule, and/or a reaction product of such a hydrocarbon polymer with an isocyanate compound of a), wherein the molar ratio of isocyanate groups of a) to hydroxyl, thiol, amine and carboxylic acid functional groups is equal to or greater than 2.5 to 1; or

ii) one or more of a heteroatom polymer having more than one carbon-to-carbon double bond unit, or other group capable of forming a carbon-to-carbon double bond, per polymer molecule, or otherwise capable of undergoing free radical reaction, formed by reaction of one or more saturated or unsaturated carboxylic acids or acid derivatives with one or more saturated or unsaturated polyols, polythiols or polyamines or compounds with a mixture of such functional groups, and having one or more functional groups capable of reacting with an isocyanate compound of a), and/or a reaction product of such a heteroatom polymer with an isocyanate compound of a); or

iii) one or more of a hydrocarbon polymer of b)i) and one or more of a heteroatom polymer of b)ii),

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c) one or more of a liquid plasticizer,
wherein a) and b)i) and b)ii) and b)iii) are soluble or dispersible in said liquid plasticizer.

24. An article of manufacture suitable for bonding to rubber, elastomeric articles and other unsaturated polymers which comprise a reinforcement material, selected from polyester, cotton, wool, silk, ramie, nylon, cellulose, rayon, polypropylene, polyethylene, polyphenylene sulfide, carbon glass, metal polyamide or ceramic in the form of filaments, fibers, films, sheets or fiber mats, and an adhesion system resulting from admixture of:

a) one or more of an isocyanate compound selected from the group consisting of polymethylene polyphenyl isocyanate, toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), meta-tetramethylylene diisocyanate, bis(4-isocyanatocyclohexyl)methane, (1,4-bis(isocyanatomethyl) cyclohexane, isophorone diisocyanate (IPDI), diphenylmethane 4,4'-diisocyanate (MDI), p-xylylene diisocyanate, toluene triisocyanate, the biuret of hexamethylene diisocyanate, the adduct of TDI with trimethylol propane, the trimers (isocyanurate ring) of TDI and HDI, copolymers of TDI and HDI; the dimer of TDI; the caprolactam, phenol, substituted phenol, or butanone oxime blocked TDI and HDI, polycarbodiimide modified MDI and polyureas of TDI, 1,4-benzene diisocyanate, dianisidine diisocyanate, 1-chlorophenyl-2,4-diisocyanate, trimethylene diisocyanate, pentamethylene diisocyanate, butylene-1,2-diisocyanate, butylene-1,4-diisocyanate, xylene diisocyanate, 2,4-cyclohexanediiisocyanate, 1,4-cyclohexanediiisocyanate, 1,1-dibutylether diisocyanate, 1,6-cyclopentane diisocyanate, 2,5-indene diisocyanate, 1,5-naphthalene diisocyanate, triphenylmethane diisocyanate, 1,12-

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diisocyanatododecane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane and 4,4'-diisocyanatodicyclohexylpropane-(2,2),

b) i) one or more of a hydrocarbon polymer having more than one carbon-to-carbon double bond unit, per polymer molecule, derived from a diene monomer selected from the group consisting of butadiene, isoprene, chloroprene and 2,3-dimethylbutadiene, 2,4-hexadiene, ethylidene norbornene, 1,4-hexadiene, dicyclopentadiene and cyclopentene and optionally comonomers selected from the group consisting of isobutylene, ethylene, propylene, butene, vinyl ethers, styrene, vinyl toluene, vinyl pyridine, acrylonitrile and acrylic and methacrylic acids, amides and esters, having more than one hydroxyl or carboxyl, thiol or amine functional group and/or a reaction product of such hydrocarbon polymer with a), wherein the molar ratio of isocyanate groups of a) to hydroxyl, thiol, amine or carboxyl functional groups is equal to or greater than 2.5:1; or

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ii) one or more of a polyester having more than one carbon-to-carbon double bond unit per polymer molecule derived from monomers selected from:

unsaturated dicarboxylic acids selected from the group consisting of maleic, itaconic, citraconic, fumaric, trans-3-hexene-dioic acids, 1-cyclopentene-1,2-dicarboxylic anhydride, and alkenyl substituted succinic anhydrides;

saturated dicarboxylic acids selected from the group consisting of succinic, phthalic, terephthalic and trimellitic acids,

saturated diols selected from the group consisting of 2,2,4-trimethyl-1,3-pentanediol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, 2,4-dimethyl-2-ethyl-1,3-hexanediol, 1,6-hexanediol, 1,5-hexanediol, 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 7-octene-1,2-diol, 5-norbornene-2,2-dimethanol, ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol, 2,2'-thiodiethanol, 1,3-propane diol, 2-methyl-1,3-propane diol, resorcinol, 1,3-dihydroxynaphthalene, cyclohexane dimethanol, 2-amino-2-ethyl-1,3-propanediol, 2,4-dihydroxybenzoic acid, and

unsaturated polyols selected from the group consisting of 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 2-octene-1,2-diol, dihydroxy fumaric acid, 5-norbornene-2,2-dimethanol, 3-allyloxy-1,2-propanediol, cis-3,5-cyclohexadiene-1,2-diol, 2,3-dihydroxypropylacrylate and methacrylate, N,N'-(1,2-dihydroxyethylene)bisacrylamide, dihydroxycinnamic acid; and

having hydroxyl, carboxyl, thiol or amine functional groups or a combination thereof; and/or a reaction product of such polyester with a), or

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iii) one or more of a hydrocarbon polymer of b)i) and one or more of a polyester of b)ii);

c) one or more of a plasticizer which is liquid at ambient temperature selected from the group consisting of organic esters; inorganic esters; amides; hydrocarbons; halogenated derivatives of organic esters; inorganic esters and hydrocarbons; epoxidized derivatives of organic esters, inorganic esters and hydrocarbons; silanes and mixtures thereof; wherein a), b)i), b)ii) are soluble or dispersible in said liquid plasticizer of c).

25. An article of manufacture suitable for bonding to rubber, elastomeric article and other unsaturated polymers which comprise reinforcement material selected from polyester fiber and polyester films and an adhesion system resulting from admixture of:

a) polymethylene polyphenyl isocyanate,

b) i) one or more of a hydrocarbon homopolymer or copolymer of 1,3-butadiene, isoprene, chloroprene and 2,3-dimethylbutadiene containing more than one carbon-to-carbon double bond unit, per polymer molecule and having one or more of a hydroxyl, carboxyl, thiol or amine functional group and/or a reactive product of such hydrocarbon polymer with a), wherein the molar ratio of isocyanate groups of a) to hydroxyl, thiol, amine or carboxyl functional groups is equal to or greater than 2.5:1; or

ii) one or more of a polyester having more than one carbon-to-carbon double bond unit per polymer molecule formed by the reaction of maleic, itaconic, or citraconic acid, anhydride or other derivatives with 2,2,4-trimethyl-1,3-pentadiol or 2-methyl-1,3-propane diol, and having hydroxyl and/or carboxyl functional groups; and/or a reaction product of such polyester with a), or

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iii) one or more of a hydrocarbon polymer of b)i) and one or more of a polyester of b)ii);

c) one or more of a plasticizer which is liquid at ambient temperature selected from the group consisting of di(2-ethylhexyl)adipate, di(2-ethylhexyl)phthalate, di(2-ethylhexyl)terephthalate, di(n-octyl)adipate, di(n-octyl)phthalate, di(n-octyl)terephthalate, di(isooctyl)adipate, di(isooctyl)phthalate, di(isooctyl)terephthalate, di(C₇-C₁₁-alkyl)adipate, di(C₇-C₁₁-alkyl)phthalate, di(C₇-C₁₁-alkyl)terephthalate, diisobutyl adipate, mixed C₄-C₁₁-alkylphthalates, diundecyl phthalate, dinonyl adipate, di(n-decyl adipate), (n-decyl, n-octyl) adipate and (2-ethylhexyl, n-octyl) adipate;

wherein a), b)i), b)ii) are soluble and dispersible in said liquid plasticizer of c).

26. An article of manufacture as in claim 23, wherein the reinforcement material is polyester, cotton, wool, silk, ramie, nylon, cellulose, rayon, polypropylene, polyethylene, polyphenylene sulfide, carbon glass, metal polyamide or ceramic in the form of filaments, fibers, films, sheets or fiber mats.

27. An article of manufacture as in claim 23, wherein the hydrocarbon polymer and/or heteroatom polymer have an average of at least three unsaturated carbon-to-carbon double bond units or other groups capable of forming carbon-to-carbon double bonds per polymer molecule.

28. An article of manufacture as in claim 23, wherein the hydrocarbon polymer has an average of at least five and the heteroatom polymer has an average of at least eight unsaturated carbon-to-carbon

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double bond units or other groups capable of forming carbon-to-carbon double bonds or otherwise capable of undergoing free radical reaction.

29. An article of manufacture as in claim 24, wherein the hydrocarbon homopolymer or copolymer has an average of at least ten unsaturated carbon-to-carbon double bond units per polymer molecule and the polyester has an average of from 3-20 unsaturated carbon-to-carbon double bond units per polymer molecule.

30. An article of manufacture as in claim 23, wherein the hydrocarbon homopolymer is a polybutadiene homopolymer.

31. An article of manufacture as in claim 23, wherein a portion of the hydroxyl, carboxyl, thiol or amine terminal functional groups on the hydrocarbon polymer are replaced with non-reactive groups.

32. An article of manufacture as in claim 31, wherein a portion of the terminal hydroxyl, carboxyl, thiol or amine terminal functional groups of the hydrocarbon polymer are replaced by acrylate, methacrylate, epoxy, vinyl, urethane, ester and/or ether groups.

33. An article of manufacture as in claim 23, wherein a portion of the carbon-carbon double bonds of the hydrocarbon polymer are replaced by epoxy groups.

34. An article of manufacture as in claim 23, wherein the hydrocarbon polymer is a polybutadiene homopolymer or copolymer with phenyl terminal groups.

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35. An article of manufacture as in claim 23, wherein the hydrocarbon polymer has an average of 0.1 to 50 reactive functional groups per polymer molecule.

36. An article of manufacture as in claim 51, wherein the molar ratio of isocyanate and isocyanate equivalent groups to reactive functional groups on the hydrocarbon polymer and/or heteroatom polymer is equal to or greater than 5:1.

37. An article of manufacture as in claim 23, wherein the molar ratio of isocyanate and isocyanate equivalent groups to reactive functional groups on the hydrocarbon polymer and/or heteroatom polymer is equal to or greater than 25:1.

38. An article of manufacture as in claim 23, wherein the molar ratio of isocyanate and isocyanate equivalent groups to reactive functional groups on the hydrocarbon homopolymer or copolymer and/or heteroatom polymer is equal to or greater than 100:1.

39. An article of manufacture as in claim 23, wherein the heteroatom polymer is

i) one or more of a polyester derived from monomers selected from:

unsaturated dicarboxylic acids selected from the group consisting of maleic, itaconic, citraconic, fumaric, trans-3-hexene-dioic acids and 1-cyclopentene-1,2-dicarboxylic anhydride, and alkenyl substituted succinic anhydrides;

saturated dicarboxylic acids selected from the group consisting of succinic, phthalic, terephthalic and trimellitic acids,

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saturated diols selected from the group consisting of 2,2,4-trimethyl-1,3-pentanediol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, 2,4-dimethyl-2-ethyl-1,3-hexanediol, 1,6-hexanediol, 1,5-hexanediol, 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 7-octene-1,2-diol, 5-norbornene-2,2-dimethanol, ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol, 2,2'-thiodiethanol, 1,3-propanediol, 2-methyl-1,3-propanediol, resorcinol, 1,3-dihydroxynaphthalene, cyclohexane dimethanol, 2-amino-2-ethyl-1,3-propanediol, 2,3-dihydroxypropylacrylate and methacrylate, dihydroxycinnamic acid, 2,4-dihydroxybenzoic acid; and

unsaturated polyols selected from the group consisting of 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 2-octene-1,2-diol, 3-allyloxy-1,2-propanediol, 5-norbornene-2,2-dimethanol, N,N'-(1,2-dihydroxyethylene)bisacrylamide, cis-3,5-cyclohexadiene-1,2-diol; dihydroxyfumaric acid and having hydroxyl, carboxyl, thiol or amine functional groups or a mixture thereof; and/or a reaction product of such polyunsaturated polyester with a),

ii) one or more of a polyamide derived from saturated polyamines selected from the group consisting of 1,6-diaminehexane, 1,2-diamino-2-methylpropane or mixtures thereof and unsaturated dicarboxylic acids as in i)

iii) one or more of a polythiol derived from saturated dithiols selected from the group consisting of 1,6-hexane dithiol, 2,2'-dithiol diethanol, dithiolaerythritol, 1,4-butanedithiol, 2,3-butanedithiol and unsaturated dicarboxylic acids as in i); or

iv) a mixture thereof.

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40. An article of manufacture as in claim 23, wherein the heteroatom polymer is a polyester derived from maleic anhydride or itaconic anhydride and a polyol selected from the group consisting of 2,2,4-trimethylpentane-1,3-diol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, 2,4-dimethyl-2-ethyl-1,3-hexanediol, 1,6-hexanediol, 1,5-hexanediol, 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol, 1,3-propanediol, cyclohexane dimethanol, 3-allyloxy-1,2-propanediol, 2-amino-2-ethyl-1,3-propanediol, glycerol, trimethylol propane, pentaerythritol, unsaturated polyols selected from the group consisting of 5-hexene-1,2-diol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 2-octene-1,2-diol, 5-norbornene-2,2-dimethanol, cis-3,5-cyclohexadiene-1,2-diol and combinations thereof.

41. An article of manufacture as in claim 23, wherein the polyester is derived from maleic, itaconic, citraconic acid or anhydride and a polyol.

42. An article of manufacture as in claim 23, wherein the plasticizer is selected from dioctylterephthalate, di(2-ethylhexyl)adipate, di(2-ethylhexyl)phthalate, di(2-ethylhexyl)terephthalate, di(n-octyl)adipate, di(n-octyl)phthalate, di(n-octyl)terephthalate, di(isooctyl)adipate, di(isooctyl)phthalate, di(isooctyl)terephthalate, di(C₇-C₁₁-alkyl)adipate, di(C₇-C₁₁-alkyl)phthalate, di(C₇-C₁₁-alkyl)terephthalate, diisobutyl adipate, mixed C₄-C₁₁-alkylphthalates, diundecyl phthalate, dinonyl adipate, di(n-decyl adipate), (n-decyl, n-octyl) adipate and (2-ethylhexyl, n-octyl) adipate; (bis-2-ethylhexyl)-terephthalate, dioctyladipate, dibutylphthalate, C₆-C₁₁-dialkylphthalate, 2,2,4-trimethyl-3-pentyl-diisobutyrate and mixtures thereof.

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43. An article of manufacture as in claim 23, wherein the carrier is a plasticizer selected from branched and straight chain C_1 - C_{22} alkyl, C_6 - C_{20} aromatic and C_7 - C_{22} alkyl aromatic adipates, phthalates, terephthalates, glutamates, azeolates, sebacates, dodecanates and phosphates.

44. A composite article comprising

a) a matrix material of a rubber, synthetic elastomer or other unsaturated polymer,

b) a reinforcement material,

wherein said reinforcement material is coated with an adhesion system resulting from admixture of:

a) an isocyanate compound having isocyanate groups and/or isocyanate equivalent groups;

b) i) one or more of a hydrocarbon polymer having more than one carbon-to-carbon double bond unit or other group capable of forming a carbon-to-carbon double bond, per polymer molecule, or otherwise capable of undergoing free radical reaction, having functional groups capable of reacting with an isocyanate compound of a) and/or a reaction product of such a hydrocarbon polymer with an isocyanate compound of a) wherein the molar ratio of isocyanate and isocyanate equivalent groups of a) to reactive functional groups is equal to or greater than 2.5 to 1; or

ii) one or more of a heteroatom polymer having more than one carbon-to-carbon double bond unit or other group capable of forming a carbon-to-carbon double bond, per polymer molecule, or otherwise capable of undergoing free radical reaction, and having functional groups capable of reacting with an isocyanate compound of a) and/or a reaction product of such a heteroatom polymer with an isocyanate compound of a); or

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iii) one or more of a hydrocarbon polymer of b)i) and one or more of a heteroatom polymer of b)ii); and

c) one or more of a liquid carrier; and

wherein a) and b)i) and b)ii) and b)iii) are soluble or dispersible in said liquid carrier.

45. A composite article as in claim 44, wherein the matrix material is selected from the group consisting of natural rubber, synthetic rubber, polyisoprene and copolymers thereof, polybutadiene and copolymers thereof, styrenebutadiene rubbers, acrylonitrilebutadiene rubbers, polychloroprene rubbers, EPDM elastomers, chlorosulfonated polyethylene elastomers, butyl elastomers, chlorobutyl elastomers, bromobutyl elastomers, fluoroelastomers, silicone rubbers, hydrogenated nitrile butadiene rubbers, and mixtures thereof, and the reinforcement material is selected from the group consisting of polyesters, cotton, wool, silk, ramie, cellulose, rayon, poly(p-phenylene terephthalamides), copolyterephthalimides, nylons, polyamides, polypropylene, polyethylene, polyphenylene sulfides, carbon glass, metals, ceramics or combinations thereof in the form of fibers, filaments, films, sheets and fiber mats.

46. A composite article of claim 44 selected from the group consisting of hoses, belts, tires and rolls.

47. A composite article as in claim 45, wherein the reinforcement material is coated with an adhesion system of claim 1 in an amount sufficient to provide from 0.05 to 5% by weight isocyanate groups, based on the weight of said reinforcement material.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/01914

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08K 5/10, 5/11, 5/20, 5/51; C08G 18/42, 18/48, 18/60, 18/62

US CL : 524/147, 151, 169, 296, 297, 300; 525/127, 128, 130, 131, 440

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/147, 151, 169, 296, 297, 300; 525/127, 128, 130, 131, 440

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
525/403, 410, 424, 455

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS and JPOABS: Polyisocyanates and OH, SH, amine or COOH polyethers, polyamides, polyesters or polydienes

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Chemical Abstracts, Accession No. CA108(4): 23193c, Czech Patent No. 235735 (SMATLOVA ET AL.) 01 December 1986.	1-47
Y	US, A, 3,837,892 (MARZOCCHI) 24 September 1974, see column 6, lines 20-24 and 36-66.	1-47
A	US, A, 4,318,959 (EVANS ET AL.) 09 March 1982, see column 13, lines 15-30; column 15, lines 58-68 and column 17, lines 21-31.	1-22
Y	US, A, 5,221,707 (CHIHARA, ET AL.) 22 June 1993, see column 2, lines 18-24; column 3, lines 16-19 and column 4, lines 32-36.	1-22
Y	JP, A, 61-255973 (IDEMITSU PETROCHEM CO. LTD) 13 November 1986, see Abstract.	1-22

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be part of particular relevance
* E		earlier document published on or after the international filing date
* L		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* O		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* &	document member of the same patent family

Date of the actual completion of the international search

24 APRIL 1995

Date of mailing of the international search report

10 JUL 1995

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/01914

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 62-32165 (IDEMITSU PETROCHEM CO. LTD) 12 February 1987, see Abstract.	1-22
Y	JP, A, 62-100513 (ITO SEIYU KK) 11 May 1987, see Abstract.	1-22
Y	JP, A, 01-16863 (IDEMITSU PETROCHEM CO. LTD) 20 January 1989, see Abstract.	1-22
Y	JP, A, 04-142325 (HITACHI CHEM CO. LTD) 15 May 1992, see Abstract.	1-22
A	JP, A, 63-120722 (YOKOHAMA RUBBER CO. LTD) 25 May 1988, see Abstract.	1-22
A	JP, A, 02-111650 (IDEMITSU PETROCHEM CO. LTD) 24 April 1990, see Abstract.	1-22
Y	JP, A, 59-227915 (NIPPON DENSHIN DENWA KOSHA) 21 December 1984, see Abstract.	1-43

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/01914

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

- I. Claims 1-22, drawn to an adhesion system classified in class 524, subclass 297.
- II. Claims 23-43, drawn to an article comprising a reinforcement material and an adhesion system classified in class 428, subclass 288.
- III. Claims 44-47, drawn to a composite article comprising a reinforcement material, an adhesion system and a matrix material classified in class 428, subclass 521.

The invention listed as Groups I-III do not meet the requirements for Unity of Invention under PCT Rule 13.1 to 13.3 because the basic chemical structure of the adhesion system (Group I) is physically and chemically changed upon blending with the reinforcement material (Group II) and the reinforcement material with the matrix material (Group III) due to the reaction between the isocyanate compound and the functional groups of the hydrocarbon or heteroatom polymer. The basic chemical structure of the invention of Group III is physically and chemically changed from the invention of Group II as a result of the vulcanization of the matrix material. Accordingly, Unity of Invention is not present in the context of intermediate and final products as described in PCT Rules, Annex B, Part 1, Section (g) (ii) (A) (1).